

Supporting Information

Iodine (III)-Catalyzed Electrophilic Nitration of Phenols via Non-Brønsted Acidic NO₂⁺ Generation

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Table of Contents

1. General Information	S2
2. Optimization of the reaction conditions	S3
3. Synthesis of nitrated phenols and phenols-ethers	S7
4. Copies of NMR ¹ H and ¹³ C Spectra	S35
5. Computational Methodology	S90
6. Cartesian Coordinates of Optimized Structures	S92

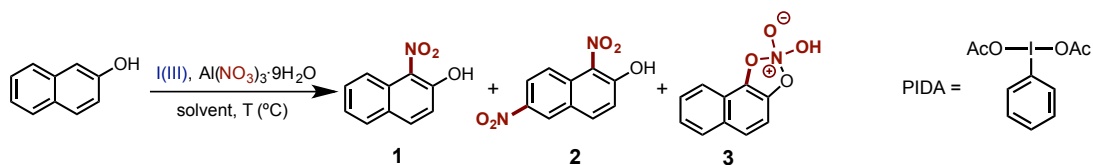
1. General Information

All moisture and oxygen sensitive reactions were carried out in flame-dried round bottom flasks or using Schlenk techniques under an inert atmosphere of nitrogen, unless otherwise specified. NMR spectra were measured on ^1H and ^{13}C NMR spectra were acquired on Bruker Advance III (500 MHz) and JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in CDCl_3 , integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sep = septet, dd = doublet-doublet, m = multiplet, b = broad), coupling constants (Hz), and assignment. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer. High-resolution mass spectra (HRMS) were performed on Bruker microTOF and Thermo Exactive plus. YMC syringe pump (model number: YSP-101) was used when slow addition of a solution was conducted. The products were purified by flash column chromatography (silica gel 60, Merck and Sigma aldrich, 230-400 mesh) or preparative thin layer chromatography silica gel (PLC 60 F254. 0.5 mm). Commercially available reagents were purchased from Wako, Aldrich, TCI and Alfa-aesar chemicals and used as received. Anhydrous solvents were purchased from Sigma Aldrich in SureSeal® bottles. Thin layer chromatography was performed with TLC Silica gel 60 F256 plates, and visualization was effected with short wavelength UV light (254 nm).

Compounds were characterized using ^1H -NMR, ^{13}C -NMR, Melting Point, IR (ATR) and Mass spectroscopy. (Copies of ^1H -NMR and ^{13}C -NMR spectra are provided in the supporting information for all new compounds). Data of known compounds were compared with existing literature characterization data and the references are given.

2. Optimization of the reaction conditions

Table S1. Optimization of the catalytic nitration of 2-naphthol by the system PhIO/M(NO₃)_n [M=Al, Na, Sr, Bi, Zn, Fe or Ag], n= 1, 2, 3.

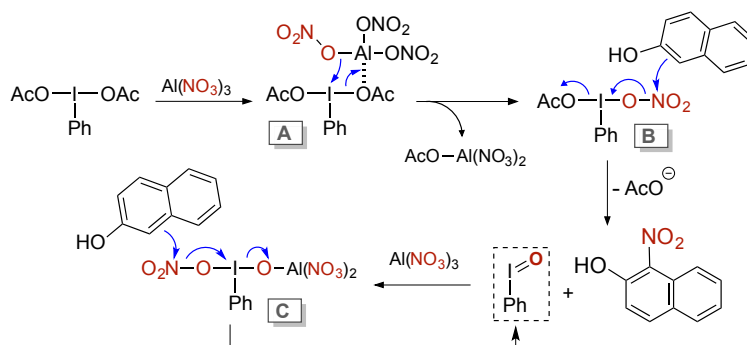


entry	I(III) (equiv)	M(NO ₃) _n , equiv	solvent	t (°C)	yield (%) ^b 1 / 2 / 3
1 ^c	PIDA (1.2)	Al(NO ₃) ₃ , 2.4	MeCN	23	0 / 91 / 0
2	PIDA (1.2)	Al(NO ₃) ₃ , 2.4	MeCN	23	0 / 88 / 0
3 ^d	PIDA (1.2)	Al(NO ₃) ₃ , 2.4	MeCN	23	<5 / 71 / 0
4 ^d	PIDA (0.5)	Al(NO ₃) ₃ , 0.35	MeCN	23	68 / <5 / 0
5 ^d	PIDA (0.3)	Al(NO ₃) ₃ , 0.35	MeCN	23	77 / <5 / 0
6 ^e	PIDA (0.25)	Al(NO ₃) ₃ , 0.35	MeCN	0	33 / 0 / 0
7 ^f	PhIO (0.1)	Al(NO ₃) ₃ , 0.35	MeCN	0	34 / 8 / <5
8 ^f	PhIO (0.15)	Al(NO ₃) ₃ , 0.35	MeCN	0	34 / 10 / <5
9	PhIO (0.2)	Al(NO ₃) ₃ , 0.35	MeCN	0	72 / 5 / 0
10	PhIO (0.25)	Al(NO₃)₃, 0.35	MeCN	0	78 / 7 / 0
11	PhIO (0.30)	Al(NO ₃) ₃ , 0.35	MeCN	0	42 / 5 / 27
12	PhIO (0.35)	Al(NO ₃) ₃ , 0.35	MeCN	0	46 / 7 / 27
13	PhIO (0.25)	Al(NO ₃) ₃ , 0.35	DCM	0	c. r. m.
14	PhIO (0.25)	Al(NO ₃) ₃ , 0.35	TFE	0	c. r. m.
15	PhIO (0.25)	Al(NO ₃) ₃ , 0.35	MeOH	0	c. r. m.
16 ^e	PhIO (0.25)	Al(NO ₃) ₃ , 0.35	THF	0	48 / 0 / 0
17 ^e	PhIO (0.25)	Al(NO ₃) ₃ , 0.35	H ₂ O	0	0 / 12 / 0
18 ^e	PhIO (0.25)	Al(NO ₃) ₃ , 0.35	DMSO	0	25 / 0 / 0
19	PhIO (0.25)	NaNO ₃ , 0.35	MeCN	0	n. r.
20	PhIO (0.25)	Sr(NO ₃) ₂ , 0.35	MeCN	0	n. r.
21	PhIO (0.25)	Zn(NO ₃) ₂ , 0.35	MeCN	0	c. r. m.
22	PhIO (0.25)	Fe(NO ₃) ₃ , 0.35	MeCN	0	c. r. m.
23	PhIO (0.25)	AgNO ₃ , 0.35	MeCN	0	c. r. m.
24	PhIO (0.25)	Bi(NO ₃) ₃ , 0.35	MeCN	0	27 / 0 / 0

25	PIDA (0.25)	--	MeCN	0	n. r.
26	PhIO (0.25)	--	MeCN	0	n. r.
27	--	0.35	MeCN	0	n. r.

^a Reaction conditions: 2-naphthol (0.5 mmol), solvent (0.3 M), open flask. ^b Isolated yields. ^c 4 Å molecular sieves were used. ^d The reaction started at 0 °C and was progressively warmed to 23 °C. ^e It was recovered 22% of the starting 2-naphthol. ^f The reaction was not complete after 10 h. c.r.m. = complex reaction mixture. n.r. = no reaction observed.

Different oxidants and metallic nitrates were used in the optimization of the nitration reaction. When we tried sub-stoichiometric amount of oxidant, we discover that the transformation proceeded until complete consumption of the starting 2-naphthol with good yield (entry 4) and few amounts of bis-nitration product. In fact, by lowering the amount of PIDA to 0.3 equiv we could improve the yield until 77%, with almost no over-nitration product found (entry 5). ***This conducted us to rationalize that a catalytic process would be involved since theoretically at least one equivalent of oxidant should be necessary to complete the reaction.*** The hypothesis argued is following outlined.



The plausible mechanism for this catalytic transformation involves aluminum coordination and cleavage of the acetoxy group in PIDA (A) followed by bond formation between a nitrate group and the I(III) center (B). Then, after the attack of the phenol at the nitrogen, the nitrated product would be released concomitant with iododibenzene (PhIO) formation. This could react again with the nitrate salt giving rise to the intermediate C which is attacked by a second molecule of 2-naphthol. Thereafter the nitration takes place and the iododibenzene is released to continue the catalytic cycle.

To our delight by using iodosylbenzene (entries 7-24) in sub-stoichiometric amounts 0.1-0.3 mol %, we observed the fully consumption of the starting 2-naphthol with the best yield for our determination in entry 10 (78%). Then to validate the role of PIDA we reproduce the optimal conditions described in entry 10 using PIDA instead of PhIO, however the starting 2-naphthol was not totally consumed, recovering 22% and with only 33% of yield for 1-nitro-2-naphthol. We support this result considering that a less active mixed aluminum salt (with the ligands AcO⁻ and NO₃⁻ competing for the iodine bond formation according to the proposed catalytic cycle) is been formed each time after the corresponding catalytic cycle. In this consideration, after of the nitronium generation, the resulting salt obtained should be AlOAc(NO₃), Al(OAc)₂NO₃ and finally Al(OAc)₃. In comparison, with the use of PhIO, the resulting aluminum salt should be Al(NO₃)₂OH, AlNO₃(OH)₂ and finally Al(OH)₃. This salt has much less steric hindrance (by comparing -OH with AcO⁻) and the thermodynamic in general for this route is favored by the formation of a precipitate [Al(OH)₃].

In regard to the reaction mechanism, the role and the necessity for using aluminum as the metallic source of nitrates was experimentally demonstrated (entries 19-24). Different metallic nitrates such as Na, Sr, Fe, Zn or Ag, showed either no reaction or a very complex reaction mixture. Indicating that there is no driven force for the NO₂⁺ formation (Na and Sr) or the main reaction take place between the metal and the 2-naphthol (Zn, Fe and Ag). Finally by using Bi(NO₃)₃ we observed a poor 27% of yield for (**1**). This is not a surprising result since is described that this salt is able to carry out nitration reactions by itself (see ref 30 of the manuscript) when is used in stoichiometric amount, nevertheless under our catalytic system is not effective.

Also, in regard to the mechanism of the reaction, we experimentally mix our starting material that is the polymeric PhIO with Al(NO₃)₃ (1:1.1) in acetonitrile. After 20 min of stir at room temperature the heterogeneous mixture was allowed to sedimentation and finally decanted. The supernatant was analyzed by HRMS, and the species present were identified. The spectra showed that the polymeric iodosylbenzene had an initial interaction with the Al(NO₃)₃ releasing its monomeric unit (PhIO) which was identified by ESI(+) as its adducts with H⁺ and MeCN-H⁺ as well as some dimeric adducts with H⁺ and MeCN-H⁺. It is described that the polymeric PhIO is broken into monomeric PhIO by Brønsted or Lewis acid reaction (Figure S1). [(a) Ochiai, M.; Miyamoto, K.; Shiro, M.; Ozawa, T.; Yamaguchi, K. *J. Am.*

Chem. Soc., **2003**, *125*, 13006-13007, (b) Wu, X.; Seo, M. S.; Davis, K. M.; Lee, Y. M.; Chen, J; Cho, K. B.; Pushkar, Y. N.; Nam, W. W., *J. Am. Chem. Soc.* **2011**, *133*, 20088].

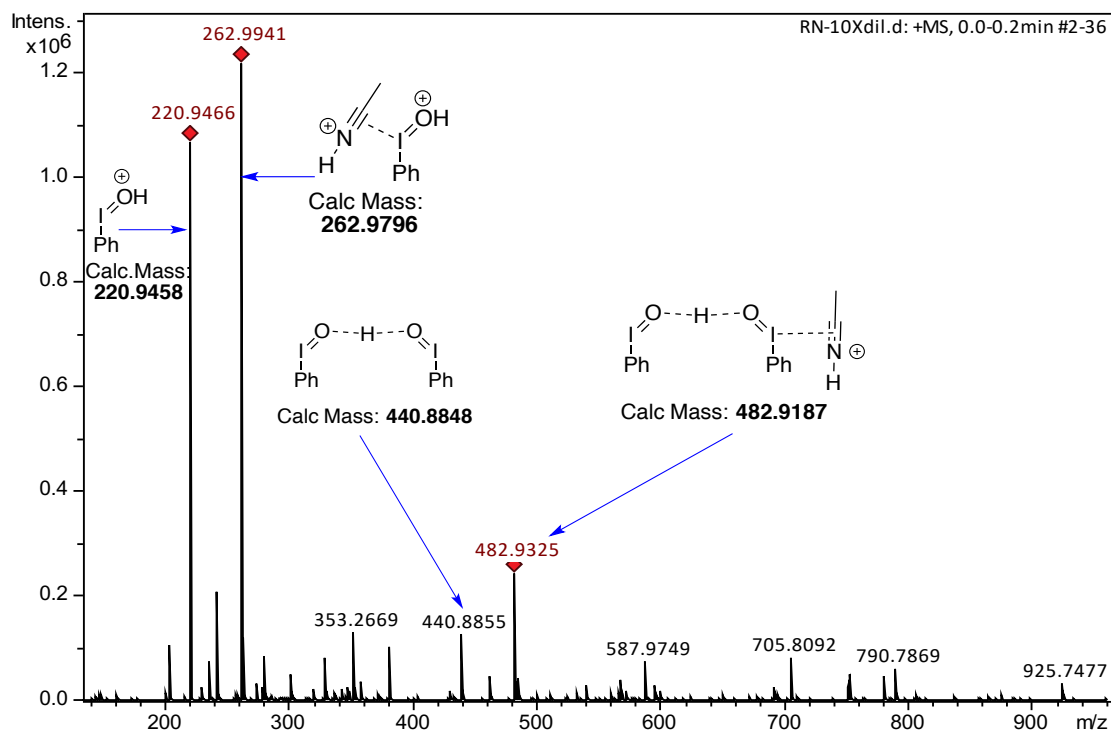
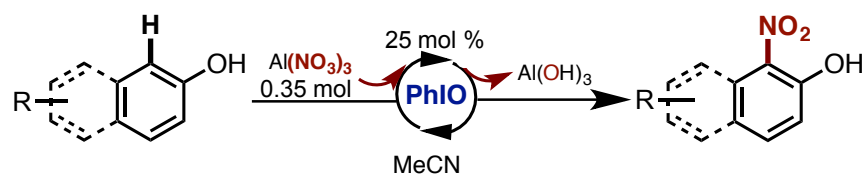


Figure S1. HRMS by ESI(+) showing the monomeric adducts of PhIO after reaction with $\text{Al}(\text{NO}_3)_3$.

3. Synthesis of nitrated phenols and phenols-ethers



General procedure A: In a 25 ml dry round-bottom flask was suspended polymeric PhIO (0.25 equiv) in dry acetonitrile at 23 °C. Then, $\text{Al}(\text{NO}_3)_3$ (0.35 equiv) was added and stirred for 10 min, afterwards it was cooled to 0 °C. The phenol derivative (1 equiv) was incorporated in one portion. The reaction was warmed to 23 °C for a period of 2-12 h until the starting phenol was fully consumed judging its advance by TLC. The reaction mixture was quenched by addition of brine (25 mL) and then extracted with EtOAc (3x10 mL). The organic extracts were collected, dried over anhydrous sodium sulfate, filtered, and concentrated in *vacuo* to remove the solvent and yield the crude of the reaction. The product was purified by column chromatography on silica gel (100-200 mesh) with EtOAc/hexane system.

General procedure B: In a 25 ml dry round-bottom flask was suspended polymeric PhIO (1.2 equiv) in dry acetonitrile at 23 °C. Then, $\text{Al}(\text{NO}_3)_3$ (2.5 equiv.) was added and stirred for 10 min. The phenol derivative (1 equiv.) was incorporated in one portion. The reaction was warmed to 23 °C for a period of 2-12 h until the starting phenol was fully consumed judging its advance by TLC. The reaction mixture was quenched by addition of brine (25 mL) and then extracted with EtOAc (3x10 mL). The organic extracts were collected, dried over anhydrous sodium sulfate, filtered, and concentrated in *vacuo* to remove solvent and yield the crude of the reaction. The product was purified by column chromatography on silica gel (100-200 mesh) with EtOAc/hexane system.

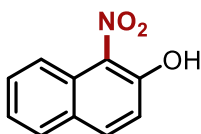
General procedure C: In a 25 ml dry round-bottom flask was suspended polymeric PhIO (0.25 equiv) in dry acetonitrile at 23 °C. Then, $\text{Al}(\text{NO}_3)_3$ (0.35 equiv.) was added and stirred for 10 min. The phenol derivative (1 equiv) was incorporated in one portion. The reaction was heated to 50 °C for a period of 2-12 h until the starting phenol was fully consumed judging its advance by TLC. The reaction mixture was quenched by addition of brine (25 mL) and then extracted with EtOAc (3x10 mL). The organic extracts were collected, dried over anhydrous sodium sulfate, filtered, and concentrated in *vacuo* to remove solvent and

yield the crude of the reaction. The product was purified by column chromatography on silica gel (100-200 mesh) with EtOAc/hexane system.

General procedure D (Gram Scale): In a 200 ml dry round-bottom flask was suspended polymeric PhIO (0.25 equiv) in dry acetonitrile at 23 °C. Then, Al(NO₃)₃ (0.35 equiv) was added and stirred for 10 min, afterwards it was cooled to 0 °C. The phenol derivative (1 equiv) was incorporated in one portion. The reaction was warmed to 23 °C for a period of 2-12 h until the starting phenol was fully consumed judging its advance by TLC. The reaction mixture was quenched by addition of brine (150 mL) and then extracted with EtOAc (3x50 mL). The organic extracts were collected, dried over anhydrous sodium sulfate, filtered, and concentrated in *vacuo* to remove the solvent and yield the crude of the reaction. The product was purified by column chromatography on silica gel (100-200 mesh) with EtOAc/hexane system.

Examples of table 1.

1-nitronaphthalen-2-ol (1)¹



67 mg of this compound were prepared according to the general procedure A in 78% of yield as yellow solid, by using the 2-naphthol as starting material.

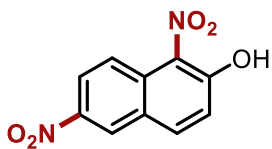
R_f = 0.90 (10% AcOEt/Hexane). m.p. = 104-106 °C. IR (neat) ν/cm⁻¹: 3241, 3056, 1622, 1541, 1245, 824, 783.

¹H NMR (500 MHz, CDCl₃): δ 12.18 (s, 1H), 8.91 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.81 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.73 (td, *J* = 8.6, 7.1, 1.3 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.0 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃): δ 159.0, 139.3, 131.1, 129.5, 128.8, 127.1, 125.8, 123.4, 119.5. HRMS (ESI-) calcd. for C₁₀H₆NO₃ [M-H]: 188.0353, found 188.0340.

¹ H. F. Jirandehi; M. Mirzaeian, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, **2011**, *41*, 284-286.

1,6-dinitronaphthalen-2-ol (2)²



106 mg of this compound were prepared according to the general procedure B in 91% of yield as yellow solid, by using the 2-naphthol as starting material.

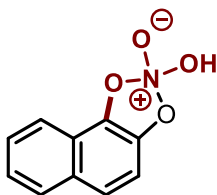
$R_f = 0.32$ (35% AcOEt/Hexane). m.p. = 189-191 °C. IR (neat) ν/cm^{-1} : 3306, 3032, 1512, 1338, 1278, 862.

^1H RMN (400 MHz, CDCl_3) δ 12.22 (s, 1H), 9.07 (dt, $J = 9.6, 0.6$ Hz, 1H), 8.75 (d, $J = 2.3$ Hz, 1H), 8.48 (dd, $J = 9.6, 2.3$ Hz, 1H), 8.18 (d, $J = 9.1$ Hz, 1H), 7.46 (d, $J = 9.6$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 160.7, 144.8, 139.8, 130.4, 127.8, 125.1, 125.1, 124.1, 122.3.

HRMS (ESI-) calcd. for $\text{C}_{10}\text{H}_5\text{N}_2\text{O}_5$ [M-H]: 233.0204, found 233.0200.

2-hydroxynaphtho[1,2-*d*][1,3,2]dioxazole 2-oxide (3)



28 mg of this compound were prepared according to the general procedure B in 27% of yield as dark red solid, by using the 2-naphthol as starting material.

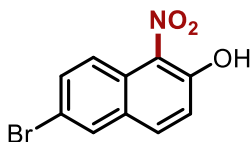
$R_f = 0.55$ (35% AcOEt/Hexane). m.p. = 121-123 °C. IR (neat) ν/cm^{-1} : 3072, 2923, 1619, 1591, 1537, 1389, 816.

^1H NMR (500 MHz, CDCl_3): δ 7.97 (d, $J = 8.9$ Hz, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.40 – 7.36 (m, 2H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.16 (d, $J = 8.3$ Hz, 1H), 5.07 (s, 1H).

^{13}C NMR (126 MHz, CDCl_3): δ 152.9, 133.5, 131.5, 129.6, 128.5, 127.6, 124.3, 124.2, 117.9, 110.9.

6-bromo-1-nitronaphthalen-2-ol (4)

² Giorgini E., R. Petrucci R., P. Astolfi P., Mason R. P., Greci L. *Eur. J. Org. Chem.* **2002**, 4011-4017.



54 mg of this compound were prepared according to the general procedure A in 41% of yield as yellow solid, by using the 6-bromo-2-naphthol as starting material.

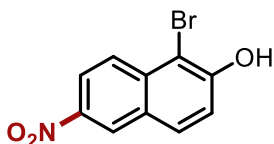
$R_f = 0.55$ (20% AcOEt/Hexane). m.p. = 121-123 °C. IR (neat) ν/cm^{-1} : 3072, 2923, 1619, 1591, 1537, 1389, 816.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 12.12 (s, 1H), 8.80 (d, $J = 9.3$ Hz, 1H), 7.97 (d, $J = 2.1$ Hz, 1H), 7.91 (d, $J = 9.1$ Hz, 1H), 7.79 (dd, $J = 9.3, 2.1$ Hz, 1H), 7.29 (d, $J = 9.1$ Hz, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 158.9, 138.0, 134.0, 131.3, 130.0, 125.7, 125.2, 121.0, 119.6.

HRMS (ESI-) calcd. for $\text{C}_{10}\text{H}_5\text{BrNO}_3$ [M-H]: 265.9458, found 265.9460.

1-bromo-6-nitronaphthalen-2-ol (5)



41 mg of this compound were prepared according to the general procedure A in 31% of yield as yellow solid, by using the 1-bromo-2-naphthol as starting material.

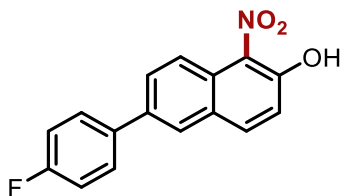
$R_f = 0.57$ (25% AcOEt/Hexane). m.p. = 122-124 °C. IR (neat) ν/cm^{-1} : 3075, 2922, 1621, 1539, 1507, 1389, 811.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 12.12 (s, 1H), 8.81 (dd, $J = 9.3, 0.5$ Hz, 1H), 7.97 (d, $J = 2.2$ Hz, 1H), 7.91 (d, $J = 9.1$ Hz, 1H), 7.79 (dd, $J = 9.3, 2.2$ Hz, 1H), 7.30 (d, $J = 9.1$ Hz, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 159.1, 138.3, 134.3, 131.6, 130.3, 126.0, 125.5, 121.2, 119.9, 100.1.

HRMS (ESI-) calcd. for $\text{C}_{10}\text{H}_5\text{BrNO}_3$ [M-H]: 266.9531, found 265.9430.

6-(4-fluorophenyl)-1-nitronaphthalen-2-ol (6)



55 mg of this compound were prepared according to the general procedure A in 39% of yield as yellow solid, by using the 6-(4-fluorophenyl)-2-naphthol as starting material.

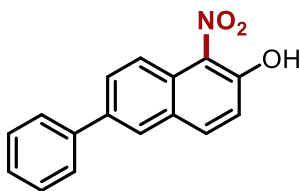
$R_f = 0.67$ (15% AcOEt/Hexane). m. p. = > 200 °C. IR (neat, ν/cm^{-1}): 3071, 2358, 1610, 1515, 1196, 827.

^1H RMN (500 MHz, CDCl_3) δ 12.22 (s, 1H), 9.00 (dd, $J = 9.0, 0.7$ Hz, 1H), 8.06 (d, $J = 9.1$ Hz, 1H), 7.98 – 7.91 (m, 2H), 7.66 (dd, $J = 8.5, 5.3$ Hz, 2H), 7.30 (d, $J = 9.0$ Hz, 1H), 7.23 – 7.16 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 163.0 (d, $J_{\text{CF}} = 248.7$ Hz), 159.0, 139.4, 137.5, 135.8 (d, $J_{\text{CF}} = 3.7$ Hz), 130.2, 129.2, 128.9 (d, $J_{\text{CF}} = 8.7$ Hz), 127.0, 126.1, 124.2, 120.1, 116.1 (d, $J_{\text{CF}} = 22.5$ Hz).

HRMS (ESI-) calcd. for $\text{C}_{16}\text{H}_9\text{FNO}_3$ [M-H]: 282.0572, found 282.0570.

1-nitro-6-phenylnaphthalen-2-ol (7)



78 mg of this compound were prepared according to the general procedure A in 59% of yield as yellow solid, by using the 6-phenyl-2-naphthol as starting material.

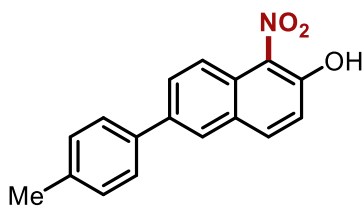
$R_f = 0.70$ (15% AcOEt/Hexane). m.p. = > 200 °C. IR (neat) ν/cm^{-1} : 3071, 2922, 1618, 1590, 1412, 816.

^1H RMN (500 MHz, CDCl_3) : δ 12.11 (s, 1H), 8.81 (dd, $J = 9.3, 0.5$ Hz, 2H), 7.97 (dd, $J = 2.0, 0.3$ Hz, 2H), 7.91 (d, $J = 9.1$ Hz, 2H), 7.79 (dd, $J = 9.3, 2.2$ Hz, 2H), 7.30 (d, $J = 9.1$ Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 158.9, 138.0, 134.0, 131.3, 130.4, 130.1, 129.2, 128.1, 127.3, 125.7, 125.3, 121.0, 120.0, 119.6.

HRMS (ESI-) calcd. for $\text{C}_{16}\text{H}_{10}\text{NO}_3$ [M-H]: 264.0666, found 264.0944.

1-nitro-6-(*p*-tolyl)naphthalen-2-ol (8)



82 mg of this compound were prepared according to the general procedure B in 59% of yield as yellow solid, by using the 6-(*p*-tolyl)-2-naphthol as starting material.

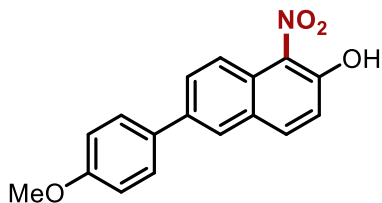
$R_f = 0.70$ (15% AcOEt/Hexane). m.p. = > 200 °C. IR (neat) ν/cm^{-1} : 3132, 2920, 1687, 1666, 1587, 1299, 837.

^1H RMN (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.0$ Hz, 1H), 7.70 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.57 – 7.53 (m, $J = 8.1$ Hz, 3H), 7.49 (d, $J = 10.1$ Hz, 1H), 7.32 (dd, $J = 7.7, 0.6$, 2H), 6.47 (d, $J = 10.1$ Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 181.3, 178.7, 148.8, 145.4, 139.6, 135.9, 135.4, 131.1, 130.1, 130.1, 128.9, 128.4, 128.4, 127.1, 21.4.

HRMS (ESI-) calcd. for $\text{C}_{17}\text{H}_{12}\text{NO}_3\text{Na}$ [M-Na]: 317.0454, found 301.9490.

6-(4-methoxyphenyl)-1-nitronaphthalen-2-ol (9)



41 mg of this compound were prepared according to the general procedure A in 28% of yield as yellow solid, by using the 6-(4-methoxyphenyl)-2-naphthol as starting material.

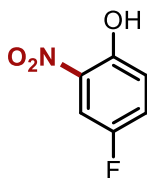
$R_f = 0.57$ (20% AcOEt/Hexane). m.p. = > 200 °C. IR (neat) ν/cm^{-1} : 3076, 2922, 1652, 1582, 1461, 811.

^1H RMN (500 MHz, CDCl_3) δ 8.15 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.67 (dt, $J = 8.1, 1.7$ Hz, 1H), 7.61 (d, $J = 1.6$ Hz, 1H), 7.59 (t, $J = 1.8$ Hz, 1H), 7.53 (t, $J = 1.5$ Hz, 1H), 7.48 (d, $J = 10.1$ Hz, 1H), 7.03 (dd, $J = 8.7, 1.6$ Hz, 2H), 6.47 (dd, $J = 10.1, 1.6$ Hz, 1H), 3.88 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 181.4, 178.6, 160.9, 148.5, 145.4, 135.5, 131.2, 131.1, 128.6, 128.4, 128.4, 128.0, 114.8, 114.8, 55.6.

HRMS (ESI-) calcd. for $\text{C}_{17}\text{H}_{12}\text{NO}_4\text{K}$ [M-K]: 334.0409, found 334.0620.

4-fluoro-2-nitrophenol (10)³



24 mg of this compound were prepared according to the general procedure A in 31% of yield as a yellow solid, by using the 4-fluorophenol as starting material.

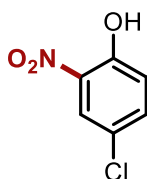
$R_f = 0.76$ (10% AcOEt/Hexane). m.p. = 74 °C. IR (neat) ν/cm^{-1} : 3315, 2970, 1691, 1479, 1393, 978.

^1H RMN (500 MHz, CDCl_3) δ 10.35 (s, 1H), 7.82 (ddd, $J = 8.2, 3.1, 0.4$ Hz, 1H), 7.44 – 7.28 (m, 1H), 7.16 (ddd, $J = 9.2, 4.6, 0.4$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 155.1 (d, $J_{\text{CF}} = 245$ Hz), 151.8 (d, $J_{\text{CF}} = 2.5$ Hz), 131.0, 125.8 (d, $J_{\text{CF}} = 23.7$ Hz), 121.5 (d, $J_{\text{CF}} = 7.5$ Hz), 110.3 (d, $J_{\text{CF}} = 27$ Hz).

HRMS (ESI-) calcd. for $\text{C}_6\text{H}_3\text{FNO}_3$ [M-H]: 156.0102, found 156.0090

4-chloro-2-nitrophenol (11)⁴



62 mg of this compound were prepared according to the general procedure A in 71% of yield as yellow solid, by using the 4-chlorophenol as starting material.

This compound was prepared according to the general procedure D in 70% of yield as yellow solid, by using 1.72 g of 4-chlorophenol as starting material.

$R_f = 0.81$ (10% AcOEt/Hexane). m.p. = 87-88 °C. IR (neat) ν/cm^{-1} : 3296, 2987, 1627, 1487, 862.

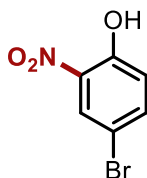
^1H RMN (500 MHz, CDCl_3) δ 10.48 (s, 1H), 8.11 (d, $J = 2.6$ Hz, 1H), 7.54 (dd, $J = 9.0, 2.6$ Hz, 1H), 7.14 (d, $J = 9.0$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.7, 137.6, 133.6, 125.2, 124.3, 121.4.

HRMS (ESI-) calcd. for $\text{C}_6\text{H}_3\text{ClNO}_3$ [M-H]: 171.9807, found 171.9750.

³ Gershon H., Clarke D. D., M. Gershon M., *Monatshefte fuer Chemie*, **1995**, 126, 1161-1166.

4-bromo-2-nitrophenol (12)⁴



74 mg of this compound were prepared according to the general procedure A in 68% of yield as yellow solid, by using the 4-bromophenol as starting material.

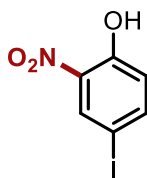
$R_f = 0.80$ (10% AcOEt/Hexane). m.p. = 92-93 °C. IR (neat) ν/cm^{-1} : 3291, 2931, 1615, 1542, 875.

^1H RMN (500 MHz, CDCl_3) δ 10.48 (s, 1H), 8.25 (d, $J = 2.4$ Hz, 1H), 7.66 (qd, $J = 9.1, 2.4, 0.3$ Hz, 1H), 7.08 (dd, $J = 9.0, 0.2$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 154.3, 140.5, 134.2, 127.5, 121.9, 111.9,

HRMS (ESI-) calcd. for $\text{C}_6\text{H}_3\text{BrNO}_3$ [M-H]: 215.9302, found 215.9290.

4-iodo-2-nitrophenol (13)⁴



86 mg of this compound were prepared according to the general procedure A in 65% of yield as yellow solid, by using the 4-iodophenol as starting material.

$R_f = 0.88$ (10% AcOEt/Hexane). m.p. = 80-82 °C. IR (neat) ν/cm^{-1} : 3261, 2923, 1609, 1572, 880.

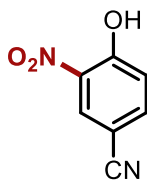
^1H RMN (500 MHz, CDCl_3) δ 10.51 (s, 1H), 8.42 (d, $J = 2.1$ Hz, 1H), 7.82 (dd, $J = 8.8, 2.1$ Hz, 1H), 6.95 (d, $J = 8.8$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 154.9, 146.0, 134.6, 133.4, 122.2, 80.5.

HRMS (ESI+) calcd. for $\text{C}_6\text{H}_4\text{BrNO}_3$ [M]: 263.9163, found 263.9142.

4-hydroxy-3-nitrobenzonitrile (14)⁴

⁴ Monzani E., Roncone R., Galliano M., Koppenol W. H., Cassela L., *Eur. J. Biochem.*, **2004**, *271*, 895-906.



58 mg of this compound were prepared according to the general procedure A in 71% of yield as yellow needles, by using the 4-hydroxybenzonitrile as starting material.

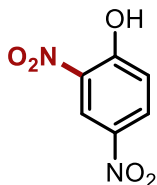
$R_f = 0.76$ (15% AcOEt/Hexane). m.p. = 141-143 °C. IR (neat) ν/cm^{-1} : 3381, 2095, 1613, 1580, 870.

^1H RMN (500 MHz, CDCl_3) δ 10.90 (s, 1H), 8.48 (d, $J = 2.0$ Hz, 1H), 7.82 (dd, $J = 8.8, 2.1$ Hz, 1H), 7.30 (d, $J = 8.8$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 157.9, 139.7, 133.6, 130.2, 121.9, 116.7, 104.7.

HRMS (ESI-) calcd. for $\text{C}_7\text{H}_3\text{N}_2\text{O}_3$ [M-H]: 163.0149, found 163.0140.

2,4-dinitrophenol (15)⁵



50 mg of this compound were prepared according to the general procedure A in 55% of yield as yellow solid, by using the 4-nitrophenol as starting material.

$R_f = 0.5$ (15% AcOEt/Hexane). m.p. = 141-143 °C. IR (neat) ν/cm^{-1} : 3305, 2913, 1633, 1598, 875.

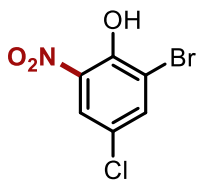
^1H RMN (500 MHz, CDCl_3) δ 11.02 (s, 1H), 9.08 (d, $J = 2.8$ Hz, 1H), 8.46 (dd, $J = 9.3, 2.8$ Hz, 1H), 7.34 (d, $J = 9.2$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 159.2, 140.4, 132.7, 131.8, 122.0, 121.4.

HRMS (ESI-) calcd. for $\text{C}_6\text{H}_3\text{N}_2\text{O}_5$ [M-H]: 183.0047, found 183.0040.

2-bromo-4-chloro-6-nitrophenol (16)

⁵ Preiss A., Elend M., Gerling S., Tränckner S., *Magn. Reson. Chem.*, **2005**, *43*, 736 – 746.



23 mg of this compound were prepared according to the general procedure A in 18% of yield as yellow solid, by using the 2-bromo-4-chlorophenol as starting material.

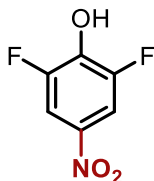
R_f = 0.79 (15% AcOEt/Hexane). m.p. = 124-126 °C. IR (neat) ν/cm^{-1} : 3186, 3062, 1516, 1301, 869.

^1H RMN (500 MHz, CDCl_3): δ 11.03 (s, 1H), 8.11 (d, J = 2.6 Hz, 1H), 7.86 (dd, J = 2.6, 0.5 Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 151.2, 140.5, 134.1, 125.5, 124.0, 114.4.

HRMS (ESI-) calcd. for $\text{C}_6\text{H}_2\text{BrClNO}_3$ [M-H]: 249.8912, found 249.8900.

2,6-difluoro-4-nitrophenol (17)



48 mg of this compound were prepared according to the general procedure A in 55% of yield as yellow solid, by using the 2,6-difluorophenol as starting material.

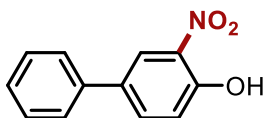
R_f = 0.78 (15% AcOEt/Hexane). m.p. = 103-105 °C. IR (neat) ν/cm^{-1} : 3177, 3092, 1611, 1509, 1343, 882.

^1H RMN (500 MHz, CDCl_3): δ 8.16 – 7.64 (m, 1H), 5.96 (s, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 150.6 (dd, J_{CF} = 249.4, 6 Hz), 139.4 (t, J_{CF} = 16 Hz), 108.8 (dt, J_{CF} = 26.2, 7.5 Hz).

HRMS (ESI-) calcd. for $\text{C}_6\text{H}_2\text{F}_2\text{NO}_3$ [M-H]: 174.0008, found 173.9990.

3-nitro-[1,1'-biphenyl]-4-ol (18)⁶



⁶ Schmidt B., Holter F., *Org. Biomol. Chem.*, **2011**, 9, 4914–4920.

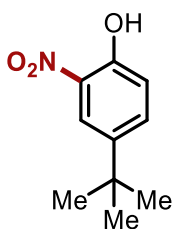
61 mg of this compound were prepared according to the general procedure A in 57% of yield as yellow solid, by using the [1,1'-biphenyl]-4-ol as starting material.

$R_f = 0.90$ (10% AcOEt/Hexane). m.p. = 65-67 °C. IR (neat) ν/cm^{-1} : 3243, 2954, 1536, 1476, 1342, 896.

^1H RMN (500 MHz, CDCl_3): δ 10.61 (s, 1H), 8.35 (d, $J = 2.3$ Hz, 1H), 7.86 (dd, $J = 8.7, 2.3$ Hz, 1H), 7.61 – 7.56 (m, 2H), 7.49 (ddd, $J = 7.8, 7.0, 0.5$ Hz, 2H), 7.45 – 7.39 (m, 1H), 7.31 – 7.27 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 154.5, 138.4, 136.4, 134.0, 129.2, 128.1, 126.8, 123.0, 120.6. HRMS (ESI-) calcd. for $\text{C}_{12}\text{H}_8\text{NO}_3$ [M-H]: 214.0510, found 214.0500.

4-(*tert*-butyl)-2-nitrophenol (19)⁷



97 mg of this compound were prepared according to the general procedure A in 89% of yield as yellow oil, by using the 4-*tert*-butylphenol as starting material.

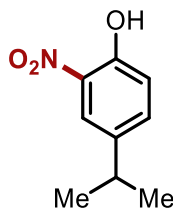
$R_f = 0.87$ (10% AcOEt/Hexane). IR (neat) ν/cm^{-1} : 3291, 1635, 1573, 1326, 816.

^1H RMN (500 MHz, CDCl_3): δ 10.45 (s, 1H), 7.91 (d, $J = 2.2$ Hz, 1H), 7.42 (dd, $J = 8.5, 0.2$ Hz, 1H), 7.07 (d, $J = 8.6$ Hz, 1H), 2.64 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 9H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.2, 143.9, 135.6, 133.2, 121.1, 119.6, 34.5, 31.2.

HRMS (ESI-) calcd. for $\text{C}_{10}\text{H}_{12}\text{NO}_3$ [M-H]: 194.0823, found 194.0810.

4-isopropyl-2-nitrophenol (20)¹⁰



⁷ Ghorbani-Choghamarani A., Goudarziafshar H., Nikoorazm M., Yousefi S., Can. J. Chem. 2009, 87, 1144-1147

63 mg of this compound were prepared according to the general procedure A in 69% of yield as yellow oil, by using the 4-isopropylphenol as starting material.

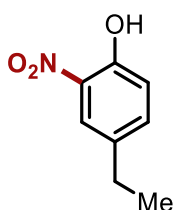
$R_f = 0.87$ (10% AcOEt/Hexane), IR (neat) ν/cm^{-1} : 3272, 1646, 1581, 1318, 849.

^1H RMN (500 MHz, CDCl_3): δ 10.45 (s, 1H), 7.93 (d, $J = 2.0$ Hz, 1H), 7.57 – 7.39 (m, 1H), 7.08 (d, $J = 8.6$ Hz, 1H), 2.91 (sep, $J = 6.9$ Hz, 1H), 1.25 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.5, 136.6, 122.0, 119.9, 100.0, 33.3, 23.8.

HRMS (ESI-) calcd. for $\text{C}_9\text{H}_{10}\text{NO}_3$ [M-H]: 180.0666, found 180.0660.

4-ethyl-2-nitrophenol (21)



56 mg of this compound were prepared according to the general procedure A in 67% of yield as yellow oil, by using the 4-ethylphenol as starting material.

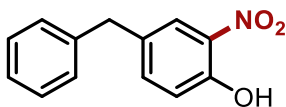
$R_f = 0.90$ (10% AcOEt/Hexane), IR (neat) ν/cm^{-1} : 3283, 1643, 1562, 1335, 811.

^1H RMN (500 MHz, CDCl_3): δ 10.45 (s, 1H), 7.91 (d, $J = 2.2$ Hz, 1H), 7.42 (dd, $J = 8.5, 0.2$ Hz, 1H), 7.07 (d, $J = 8.6$ Hz, 1H), 2.64 (q, $J = 7.6$ Hz, 2H), 1.24 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.5, 137.9, 136.6, 123.4, 119.9, 119.9, 100.1, 27.8, 15.4.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_8\text{NO}_3$ [M-H]: 166.0510, found 166.0500.

4-benzyl-2-nitrophenol (22)



101 mg of this compound were prepared according to the general procedure A in 88% of yield as yellow solid, by using the 4-benzylphenol as starting material.

2.84 g of this compound were prepared according to the general procedure D in 73% of yield as yellow solid, by using 4-benzylphenol as starting material.

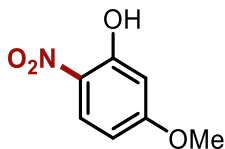
$R_f = 0.78$ (10% AcOEt/Hexane). m.p. = 60-63°C. IR (neat) ν/cm^{-1} : 3301, 3054, 1596, 1432, 1396, 865.

^1H RMN (500 MHz, CDCl_3): δ 10.49 (s, 1H), 7.93 (d, $J = 2.1$ Hz, 1H), 7.41 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.32 (t, $J = 7.4$ Hz, 2H), 7.24 (t, $J = 7.4$ Hz, 1H), 7.17 (d, $J = 7.1$ Hz, 2H), 7.08 (d, $J = 8.6$ Hz, 1H), 3.96 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.8, 139.8, 138.5, 133.8, 128.9, 126.8, 124.6, 120.2, 40.8.

HRMS (ESI-) calcd. for $\text{C}_{13}\text{H}_{10}\text{NO}_3$ [M-H]: 228.0666, found 228.0651.

5-methoxy-2-nitrophenol (23)



21 mg of this compound were prepared according to the general procedure A in 25% of yield as yellow solid, by using the 3-methoxyphenol as starting material.

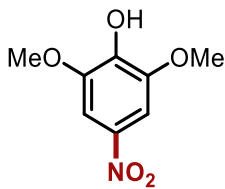
$R_f = 0.85$ (10% AcOEt/Hexane). m.p. = 83-84 °C. IR (neat) ν/cm^{-1} : 3281, 3127, 2972, 2814, 1568, 1301, 823.

^1H RMN (500 MHz, CDCl_3): δ 11.04 (s, 1H), 8.03 (dt, $J = 9.9, 1.4$ Hz, 1H), 6.82 – 6.24 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 167.2, 158.1, 127.1, 109.6, 101.6, 100.1, 56.3.

HRMS (ESI-) calcd. for $\text{C}_7\text{H}_6\text{NO}_4$ [M-H]: 168.0302, found 168.0290.

2,6-dimethoxy-4-nitrophenol (24)⁸



80 mg of this compound were prepared according to the general procedure A in 81% of yield as yellow solid, by using the 2,6-dimethoxyphenol as starting material.

$R_f = 0.84$ (10% AcOEt/Hexane). m.p. = >200 °C. IR (neat) ν/cm^{-1} : 3390, 2984, 1552, 1497, 795.

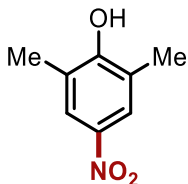
^1H RMN (500 MHz, CDCl_3): δ 7.57 (s, 2H), 6.09 (s, 1H), 3.98 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 146.5, 141.1, 140.5, 101.6, 56.8.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_8\text{NO}_5$ [M-H]: 198.0408, found 198.0260.

⁸ Koley D. Colón O. C., Savinov S., *Org. Lett.*, **2009**, *11*, 4172-4175.

2,6-dimethyl-4-nitrophenol (25)¹



46 mg of this compound were prepared according to the general procedure A in 55% of yield as yellow solid, by using the 2,6-dimethoxyphenol as starting material.

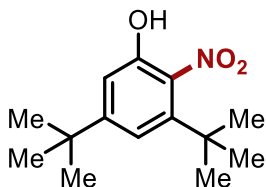
$R_f = 0.84$ (10% AcOEt/Hexane). m.p. = 171-173 °C. IR (neat) ν/cm^{-1} : 3250, 3008, 2905, 1610, 829.

^1H RMN (500 MHz, CDCl_3): δ 7.93 (s, 1H), 7.72 (s, 1H), 5.34 (s, 1H), 2.32 (s, H).

^{13}C NMR (125 MHz, CDCl_3) δ 157.9, 139.1, 135.8, 129.8, 124.6, 123.8, 100.1, 16.1.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_8\text{NO}_5$ [M-H]: 166.0510, found 166.0500.

3,5-di-*tert*-butyl-2-nitrophenol (26)⁹



31 mg of this compound were prepared according to the general procedure A in 25% of yield as yellow solid, by using the 3,5-di-*tert*-butylphenol as starting material.

$R_f = 0.85$ (10% AcOEt/Hexane). m.p. = 160-162 °C. IR (neat) ν/cm^{-1} : 3386, 2998, 1545, 1503, 871.

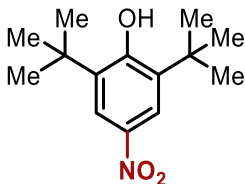
^1H RMN (500 MHz, CDCl_3): δ 6.93 (d, $J = 2.2$ Hz, 1H), 6.21 (d, $J = 2.3$ Hz, 1H), 1.27 (s, 9H), 1.23 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3) δ 181.3, 180.2, 175.3, 150.1, 133.6, 122.3, 36.2, 35.6, 29.4, 28.0.

HRMS (ESI-) calcd. for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ [M-H]: 250.1449, found 250.1390.

2,6-di-*tert*-butyl-4-nitrophenol (27)¹¹

⁹ Cross, G. G., Fischer, A., Henderson, G. N., *Can. J. Chem.*, **1984**, 62, 2803–2812.



71 mg of this compound were prepared according to the general procedure A in 57% of yield as yellow solid, by using the 2,6-di-*tert*-butylphenol as starting material.

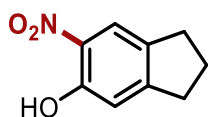
R_f = 0.86 (10% AcOEt/Hexane). m.p. = 159-162 °C. IR (neat) ν/cm^{-1} : 3380, 2995, 1563, 1516, 880.

^1H RMN (500 MHz, CDCl_3): δ 8.12 (s, 2H), 5.92 (s, 1H), 1.48 (s, 18H).

^{13}C NMR (125 MHz, CDCl_3) δ 159.7, 140.9, 136.8, 121.5, 34.7, 30.1.

HRMS (ESI-) calcd. for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ [M-H]: 250.1449, found 250.1440.

6-nitro-2,3-dihydro-1*H*-inden-5-ol (28)



69 mg of this compound were prepared according to the general procedure A in 77% of yield as yellow solid, by using the 2,3-dihydro-1*H*-inden-5-ol as starting material.

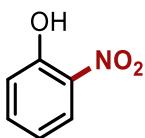
R_f = 0.87 (15% AcOEt/Hexane), m.p. = 78-79 °C. IR (neat) ν/cm^{-1} : 3168, 2959, 2922, 2849, 1634, 1525, 1255, 856.

^1H RMN (500 MHz, CDCl_3): δ 10.72 (s, 1H), 7.91 (s, 1H), 6.98 (s, 1H), 2.93 (td, J = 7.7, 1.0 Hz, 2H), 2.88 (td, J = 7.7, 1.0 Hz, 2H), 2.12 (quin, J = 7.5 Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 156.6, 154.9, 136.9, 119.9, 114.1, 100.1, 33.6, 31.7, 25.8

HRMS (ESI-) calcd. for $\text{C}_9\text{H}_8\text{NO}_3$ [M-H]: 178.0510, found 178.044.

2-nitrophenol (29)

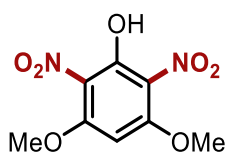


44 mg of this compound were prepared according to the general procedure B in 64% of yield as orange solid, by using the phenol as starting material.

R_f = 0.6 (10% AcOEt/Hexane). m.p. = 45-46 °C. IR (neat) ν/cm^{-1} : 3212, 3095, 1615, 1579, 1317, 1164.

^1H RMN (400 MHz, Acetone- d_6): δ 10.45 (s, 1H), 8.12 (dd, J = 8.5, 1.6 Hz, 1H), 7.71 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.21 (dd, J = 8.4, 1.2 Hz, 1H), 7.10 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H).
 ^{13}C NMR (101 MHz, Acetone- d_6) δ 155.5, 138.4, 126.0, 121.2, 120.8.
HRMS (ESI-) calcd. for $\text{C}_6\text{H}_4\text{NO}_3$ [M-H]: 138.0197, found 138.0089.

3,5-dimethoxy-2,4-dinitrophenol (30)



63 mg of this compound were prepared according to the general procedure B in 52% of yield as orange solid, by using the 3,5-dimethoxyphenol as starting material.

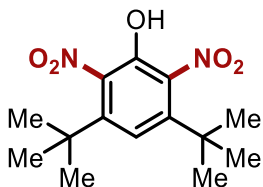
R_f = 0.35 (35% AcOEt/Hexane). m.p. = 156-157 °C. IR (neat) ν/cm^{-1} : 3180, 3060, 1868, 1771, 1580, 1320, 873.

^1H RMN (500 MHz, CDCl_3): δ 5.85 (s, 2H), 3.82 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 187.0, 176.8, 157.5, 107.6, 56.6.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_7\text{N}_2\text{O}_7$ [M-H]: 243.0259, found 243.0224.

3,5-di-*tert*-butyl-2,4-dinitrophenol (31)¹³



102 mg of this compound were prepared according to the general procedure B in 69% of yield as yellow solid, by using the 3,5-di-*tert*-butylphenol as starting material.

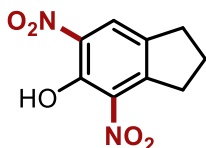
R_f = 0.36 (35% AcOEt/Hexane). m.p. = > 200 °C. IR (neat) ν/cm^{-1} : 3467, 2965, 2870, 1574, 1540, 1367, 790.

^1H RMN (500 MHz, CDCl_3): δ 7.31 (s, 1H), 1.41 (s, 18H).

^{13}C NMR (125 MHz, CDCl_3) δ 145.4, 143.0, 138.9, 120.1, 36.9, 30.7.

HRMS (ESI-) calcd. for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_5$ [M-H]: 295.1299, found 295.1290.

4,6-dinitro-2,3-dihydro-1*H*-inden-5-ol (32)



82 mg of this compound were prepared according to the general procedure B in 73% of yield as orange solid, by using the 2,3-dihydro-1*H*-inden-5-ol as starting material.

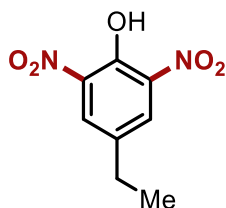
$R_f = 0.46$ (35% AcOEt/Hexane). m.p.= 105-107°C. IR (neat) ν/cm^{-1} : 3187, 2967, 1578, 1312, 1017, 732.

^1H RMN (500 MHz, CDCl_3): δ 11.25 (s, 1H), 8.11 (s, 1H), 3.17 (t, $J = 7.6$ Hz, 2H), 3.00 (t, $J = 7.6$ Hz, 2H), 2.22 (quin, $J = 7.6$ Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 149.3, 147.8, 137.2, 133.8, 123.2, 100.0, 33.2, 32.3, 25.2.

HRMS (ESI-) calcd. for $\text{C}_9\text{H}_7\text{N}_2\text{O}_5$ [M-H]: 223.0360, found 223.0353.

4-ethyl-2,6-dinitrophenol (33)



61 mg of this compound was prepared according to the general procedure B in 58% of yield as yellow solid, by using the 4-ethylphenol as starting material.

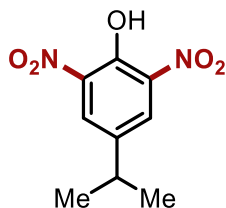
$R_f = 0.49$ (35% AcOEt/Hexane). m.p.= 76-77 °C. IR (neat) ν/cm^{-1} : 3195, 2976, 1598, 1348, 1015, 796.

^1H RMN (500 MHz, CDCl_3): δ 11.27 (s, 1H), 8.15 (d, $J = 0.5$ Hz, 2H), 2.74 (q, $J = 7.6$ Hz, 2H), 1.30 (td, $J = 7.6, 1.2$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.7, 137.5, 135.7, 130.7, 27.7, 14.9.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_7\text{N}_2\text{O}_5$ [M-H]: 211.0360, found 211.0353.

4-isopropyl-2,6-dinitrophenol (34)



73 mg of this compound were prepared according to the general procedure B in 65% of yield as yellow solid, by using the 4-isopropylphenol as starting material.

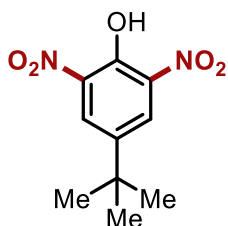
$R_f = 0.49$ (35% AcOEt/Hexane). m.p. = 89-91 °C. IR (neat) ν/cm^{-1} : 3172, 2961, 1538, 1322, 1063, 772.

^1H RMN (500 MHz, CDCl_3): δ 11.28 (s, 1H), 8.18 (s, 2H), 3.01 (sep, 1H), 1.31 (t, $J = 1.4$ Hz, 3H), 1.30 (t, $J = 1.4$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.71, 140.51, 129.51, 33.34, 23.60.

HRMS (ESI-) calcd. for $\text{C}_9\text{H}_9\text{N}_2\text{O}_5$ [M-H]: 225.0517, found 225.0509.

4-*tert*-butyl-2,6-dinitrophenol (35)



73 mg of this compound were prepared according to the general procedure B in 61% of yield as yellow solid, by using the 4-*tert*-butylphenol as starting material.

$R_f = 0.41$ (35% AcOEt/Hexane). m.p. = 95-97 °C. IR (neat) ν/cm^{-1} : 3215, 3009, 2924, 1542, 1380, 720.

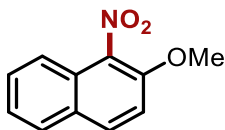
^1H RMN (500 MHz, CDCl_3): δ 11.29 (s, 1H), 8.32 (s, 2H), 1.38 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.3, 143.1, 137.3, 128.5, 34.9, 30.9.

HRMS (ESI-) calcd. for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_5$ [M-H]: 239.0673, found 239.0668.

Examples of table 2.

2-methoxy-1-nitronaphthalene (36)¹⁰



28 mg of this compound were prepared according to the general procedure A in 27% of yield as yellow solid, by using the 2-methoxynaphthalene as starting material.

¹⁰ Mascall M.; Yin L.; Edwards R.; Jarosh M. *J. Org. Chem.* **2008**, *73*, 6148-6151

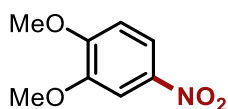
$R_f = 0.85$ (15% AcOEt/Hexane). m.p. = 127-128 °C. IR (neat) ν/cm^{-1} : 1609, 1596, 1480, 1250, 1321, 960.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.73 (dd, $J = 1.5, 0.5$ Hz, 1H), 8.21 (ddd, $J = 9.0, 2.3, 1.3$ Hz, 1H), 7.91 (dd, $J = 9.0, 0.5$ Hz, 1H), 7.81 (dd, $J = 9.0, 0.5$ Hz, 1H), 7.28 (ddd, $J = 9.0, 2.5, 1.3$ Hz, 1H), 7.20 (d, $J = 2.2$ Hz, 1H), 3.97 (s, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 148.7, 132.2, 129.2, 128.3, 128.1, 125.8, 125.2, 120.5, 113.2, 100.0, 57.1.

HRMS (ESI+) calcd. for $\text{C}_{11}\text{H}_9\text{NO}_3$ [M+H]: 204.0655, found 204.0657.

1,2-dimethoxy-4-nitrobenzene (37)¹¹



62 mg of this compound were prepared according to the general procedure C in 68% of yield as pale yellow crystals, by using the 1,2-dimethoxybenzene as starting material.

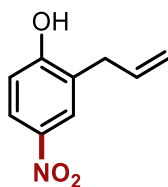
$R_f = 0.9$ (10% AcOEt/Hexane). m.p. = 97-99 °C. IR (neat) ν/cm^{-1} : 2992, 2947, 2915, 1608, 1570, 879.

$^1\text{H RMN}$ (500 MHz, CDCl_3) δ 7.92 (ddd, $J = 8.9, 2.6, 0.8$ Hz, 1H), 7.75 (d, $J = 2.6$ Hz, 1H), 6.91 (d, $J = 8.9$ Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 154.6, 149.0, 141.6, 117.9, 110.0, 106.6, 56.6, 56.4.

HRMS (ESI+) calcd. for $\text{C}_8\text{H}_9\text{NO}_4$ [M+H]: 183.0532, found 183.0290.

2-allyl-4-nitrophenol (38)¹²



51 mg of this compound were prepared according to the general procedure A in 57% of yield as yellow oil, by using the 2-allylphenol as starting material.

$R_f = 0.87$ (10% AcOEt/Hexane), IR (neat) ν/cm^{-1} : 3268, 2985, 1640, 1621, 1591, 853.

¹¹ Dhakshinamoorthy A., Sharmila A., Pitchumani K. *Chem. Eur. J.* **2010**, *16*, 1128 – 1132.

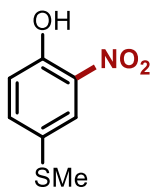
¹² van Otterlo W. A. L., Morgans, G. L. Madeley L. G., Kuzvidza S., Moleele S. S., Thornton N., B. de Koning C. *Tetrahedron*, 2005, *61*, 7746–7755.

^1H RMN (500 MHz, CDCl_3): δ 10.94 (s, 1H), 8.00 (ddd, $J = 8.6, 1.0, 0.6$ Hz, 1H), 7.59 – 7.40 (m, 1H), 6.92 (dd, $J = 8.5, 7.4$ Hz, 1H), 5.99 (dddd, $J = 16.8, 10.5, 7.0, 6.3$ Hz, 1H), 5.25 – 4.91 (m, 2H), 3.49 (d, $J = 6.7$ Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.4, 137.6, 135.2, 131.5, 123.2, 119.6, 116.9, 100.0, 33.8.

HRMS (ESI-) calcd. for $\text{C}_9\text{H}_8\text{NO}_5$ [M-H]: 178.0510, found 178.0500.

4-(methylthio)-2-nitrophenol (39)



26 mg of this compound were prepared according to the general procedure A in 28% of yield as yellow solid, by using the 4-methylthiophenol as starting material.

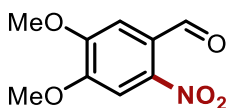
$R_f = 0.85$ (10% AcOEt/Hexane). m.p. = 83-84 °C. IR (neat) ν/cm^{-1} : 3405, 3196, 2927, 1521, 1246, 793.

^1H RMN (500 MHz, CDCl_3): δ 10.48 (s, 1H), 7.96 (d, $J = 2.4$ Hz, 1H), 7.51 (dd, $J = 8.8, 2.4$ Hz, 1H), 7.10 (d, $J = 8.8$ Hz, 1H), 2.50 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.4, 137.6, 130.6, 122.8, 120.7, 100.06, 17.1.

HRMS (ESI-) calcd. for $\text{C}_7\text{H}_6\text{NO}_3\text{S}$ [M-H]: 184.0074, found 184.0070.

4,5-dimethoxy-2-nitrobenzaldehyde (40)¹³



24 mg of this compound were prepared according to the general procedure C in 23% of yield as yellow solid, by using the 3,4-dimethoxybenzaldehyde as starting material.

$R_f = 0.62$ (30% AcOEt/Hexane). m.p. = 130-132 °C. IR (neat) ν/cm^{-1} : 2967, 2893, 1675, 1510, 862.

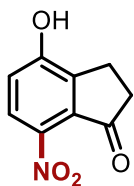
^1H RMN (500 MHz, CDCl_3) δ 10.46 (d, $J = 0.8$ Hz, 1H), 7.62 (s, 1H), 7.43 (s, 1H), 4.04 (s, 3H), 4.03 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 187.8, 153.4, 152.6, 125.7, 109.9, 107.3, 57.0, 56.9.

¹³ Bunce N. J., Stephenson K. L.. *Can. J. Chem.* **1989**, *67*, 220-226.

HRMS (ESI+) calcd. for C₉H₁₀NO₅ [M+H]: 212.0553, found 212.0560.

4-hydroxy-5-nitro-2,3-dihydro-1*H*-inden-1-one (41)



42 mg of this compound were prepared according to the general procedure A in 44% of yield as yellow solid, by using the 4-hydroxy-2,3-dihydro-1*H*-inden-1-one as starting material.

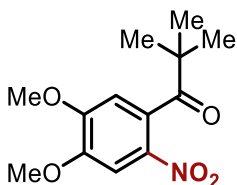
R_f = 0.66 (20% AcOEt/Hexane). m.p. = 92-94 °C. IR (neat) v/cm⁻¹: 3280, 3102, 2955, 1706, 1612, 1519, 1233, 890.

¹H RMN (500 MHz, CDCl₃): δ 10.77 (s, 1H), 8.14 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.33 (dd, *J* = 8.6, 0.5 Hz, 1H), 3.19 (dd, *J* = 5.9, 5.5 Hz, 2H), 2.91 – 2.69 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 205.2, 153.2, 146.4, 143.9, 125.1, 114.4, 36.6, 22.7.

HRMS (ESI-) calcd. for C₉H₆NO₄ [M-H]: 192.0302, found 192.02880.

1-(4,5-dimethoxy-2-nitrophenyl)-2,2-dimethylpropan-1-one (42)



93 mg of this compound were prepared according to the general procedure C in 70% of yield as yellow solid, by using the 1-(3,4-dimethoxyphenyl)-2,2-dimethylpropan-1-one as starting material.

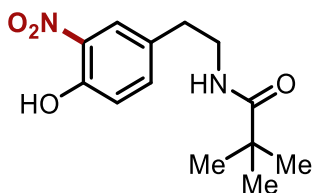
R_f = 0.48 (20% AcOEt/Hexane). m.p. = 79-81 °C. IR (neat) v/cm⁻¹: 2918, 2859, 1736, 1521, 834.

¹H RMN (500 MHz, CDCl₃) δ 7.70 (s, 1H), 6.58 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 1.26 (s, 9H).

¹³C NMR (125 MHz, CDCl₃) δ 210.4, 154.3, 149.1, 132.3, 108.1, 106.8, 100.1, 56.7, 56.6, 45.5, 27.4.

HRMS (ESI+) calcd. for C₁₃H₁₈NO₅ [M+H]: 268.1179, found 268.1179.

N-(4-hydroxy-3-nitrophenethyl)pivalamide (43)



78 mg of this compound were prepared according to the general procedure C in 59% of yield as yellow solid, by using the *N*-(4-hydroxyphenethyl)pivalamide as starting material.

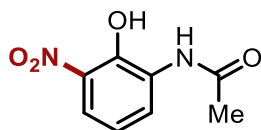
$R_f = 0.70$ (20% AcOEt/Hexane). m.p. = 105-106 °C: 106-108 °C. IR (neat) ν/cm^{-1} : 3407, 3290, 2934, 1634, 1532, 817.

^1H RMN (500 MHz, CDCl_3): δ 10.47 (d, $J = 1.1$ Hz, 1H), 7.91 (s, 1H), 7.43 (d, $J = 8.7$ Hz, 1H), 7.11 (dd, $J = 8.6, 1.1$ Hz, 1H), 5.66 (s, 1H), 3.47 (q, $J = 5.9$ Hz, 2H), 2.82 (t, $J = 7.0$ Hz, 2H), 1.15 (s, 10H).

^{13}C NMR (125 MHz, CDCl_3) δ 178.7, 154.0, 138.5, 131.6, 124.6, 120.3, 100.1, 40.6, 38.8, 34.7, 27.7.

HRMS (ESI-) calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_4$ [M-H]: 265.1194, found 265.1190.

***N*-(2-hydroxy-3-nitrophenyl)acetamide (44)**



19 mg of this compound were prepared according to the general procedure C in 20% of yield as yellow solid, by using the 1-(3,4-dimethoxyphenyl)-2,2-dimethylpropan-1-one as starting material.

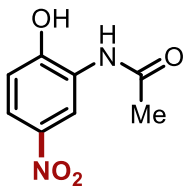
$R_f = 0.40$ (20% AcOEt/Hexane). m.p. = 85-87 °C. IR (neat) ν/cm^{-1} : 3330, 2976, 1692, 1553, 810.

^1H RMN (500 MHz, CDCl_3) δ 11.06 (s, 1H), 8.72 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.81 (dd, $J = 8.7, 1.5$ Hz, 2H), 7.07 – 6.91 (m, 1H), 2.26 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 168.7, 144.3, 133.3, 129.3, 126.9, 120.2, 118.7, 29.8, 25.0.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_7\text{N}_2\text{O}_4$ [M-H]: 195.0411, found 195.0387.

***N*-(2-hydroxy-5-nitrophenyl)acetamide (45)**



22 mg of this compound were prepared according to the general procedure C in 23% of yield as yellow solid, by using the 1-(3,4-dimethoxyphenyl)-2,2-dimethylpropan-1-one as starting material.

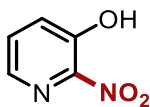
$R_f = 0.42$ (20% AcOEt/Hexane). m.p. = 84-86 °C. IR (neat) ν/cm^{-1} : 3341, 2963, 1686, 1557, 896.

^1H RMN (500 MHz, CDCl_3) δ 8.00 (s, 1H), 7.58 (dd, $J = 2.2, 1.5$ Hz, 1H), 6.93 – 6.34 (m, 2H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 188.0, 182.8, 169.3, 138.3, 138.3, 133.2, 115.0, 100.1, 25.0.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_7\text{N}_2\text{O}_4$ [M-H]: 196.0411, found 195.0393.

2-nitropyridin-3-ol (46)¹⁴



42 mg of this compound were prepared according to the general procedure C in 60% of yield as yellow solid, by using the pyridin-3-ol as starting material.

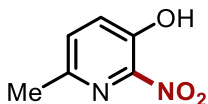
$R_f = 0.54$ (25% AcOEt/Hexane). m.p. = 69-70°C. IR (neat) ν/cm^{-1} : 2992, 2864, 1607, 1553, 1479, 886.

^1H RMN (500 MHz, CDCl_3): δ 10.22 (s, 1H), 8.22 (dd, $J = 4.1, 1.8$ Hz, 1H), 7.64 (dddd, $J = 9.2, 4.7, 2.9, 0.6$ Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 151.1, 140.5, 132.2, 130.2, 100.1.

HRMS (ESI-) calcd. for $\text{C}_5\text{H}_3\text{N}_2\text{O}_3$ [M-H]: 139.0149, found 139.0136.

6-methyl-2-nitropyridin-3-ol (47)¹⁴



¹⁴ de Selms, R. C. *J. Org. Chem.*, **1968**, *33*, 478–480.

64 mg of this compound were prepared according to the general procedure C in 83% of yield as yellow solid, by using the 6-methylpyridin-3-ol as starting material.

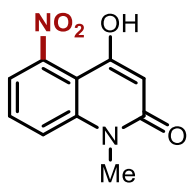
$R_f = 0.5$ (25% AcOEt/Hexane). m.p. = 105-107 °C. IR (neat) ν/cm^{-1} : 2915, 9862, 1607, 1546, 1290, 870.

^1H RMN (500 MHz, CDCl_3): δ 10.11 (s, 1H), 7.53 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.46 (dd, $J = 8.5, 1.9$ Hz, 1H), 2.58 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 150.11, 149.14, 132.58, 130.40, 100.06, 77.16, 23.44.

HRMS (ESI-) calcd. for $\text{C}_6\text{H}_5\text{N}_2\text{O}_3$ [M-H]: 153.0306, found 153.0293.

4-hydroxy-1-methyl-5-nitroquinolin-2(1H)-one (48)



12 mg of this compound were prepared according to the general procedure C in 11% of yield as yellow solid, by using the 4-hydroxy-1-methylquinolin-2(1H)-one as starting material.

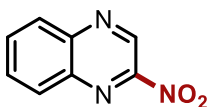
$R_f = 0.54$ (30% AcOEt/Hexane). m.p. = >200 °C. IR (neat) ν/cm^{-1} : 3059, 2922, 2852, 1780, 1718, 1604, 1324, 863, 758.

^1H RMN (500 MHz, CDCl_3): δ 7.64 – 7.57 (m, 2H), 7.13 (td, $J = 7.6, 0.8$ Hz, 1H), 6.89 (dd, $J = 8.4, 0.8$ Hz, 1H), 3.25 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 183.47, 158.39, 151.63, 138.51, 125.44, 123.98, 117.64, 110.04, 100.06, 26.36.

HRMS (ESI-) calcd. for $\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4$ [M-H]: 219.0411, found 219.0405.

2-nitroquinoxaline (49)



52 mg of this compound were prepared according to the general procedure C in 60% of yield as yellow solid, by using the quinoxaline as starting material.

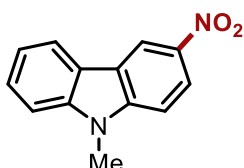
$R_f = 0.54$ (25% AcOEt/Hexane). m.p. = 140-142°C. IR (neat) ν/cm^{-1} : 3052, 1595, 1532, 1510, 1328, 805.

^1H RMN (500 MHz, CDCl_3): δ 9.07 – 8.99 (m, 3H), 8.56 (ddd, $J = 9.2, 2.5, 0.6$ Hz, 1H), 8.29 (d, $J = 9.2$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.8, 147.2, 145.5, 142.1, 131.5, 126.2, 123.6, 116.4.

HRMS (ESI+) calcd. for $\text{C}_8\text{H}_6\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]$: 176.0445, found 176.0456.

9-methyl-3-nitrocarbazole (50)



65 mg of this compound were prepared according to the general procedure C in 57% of yield as yellow solid, by using the 9-methylcarbazole as starting material.

$R_f = 0.63$ (15% AcOEt/Hexane). m.p. = 168–171 °C. IR (neat) ν/cm^{-1} : 3018, 2960, 1650, 1593, 1324, 745.

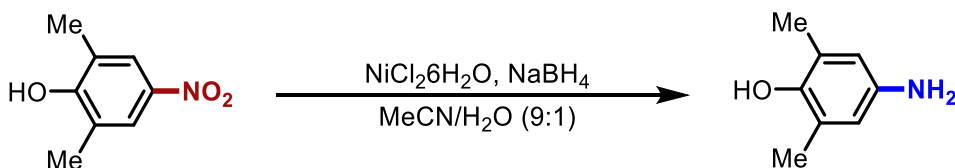
^1H RMN (500 MHz, CDCl_3): δ 9.03 (d, $J = 2.2$ Hz, 1H), 8.41 (dd, $J = 9.0, 2.3$ Hz, 1H), 8.17 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.59 (ddd, $J = 8.3, 7.2, 1.1$ Hz, 1H), 7.48 (d, $J = 8.2$ Hz, 1H), 7.42 (d, $J = 9.0$ Hz, 1H), 7.39 – 7.34 (m, 1H), 3.93 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 144.0, 142.2, 140.7, 127.5, 122.8, 122.5, 121.7, 121.0, 120.9, 117.3, 109.5, 108.1, 29.6.

HRMS (ESI+) calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]$: 227.0815, found 227.0811.

Examples of scheme 1.

4-amino-2,6-dimethylphenol (51)¹⁵



The following compound was obtained by the reduction of nitro group by using 2,6-dimethyl-4-nitrophenol in 91% yield as 63 mg of yellow solid. In a round-bottom flask the nitro compound **22** (0.5 mmol) was dissolved. $\text{NiCl}_2 \cdot 9\text{H}_2\text{O}$ (0.2 equiv) was added to the mixture and the reaction was cooled at 0 °C. NaBH_4 (4 equiv) was slowly added to the mixture. The

¹⁵ Guerra J. P. T. A., Lindner A., Nicoletti C. R., Marini V. G., Silva M., Machado V. G., *Tetrahedron Letters*, **2015**, 56, 4733-4736.

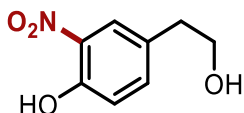
reaction was carried out to room temperature and monitored by TLC until **22** was finished. The reaction was stopped by adding brine. Was extracted with ethyl acetate (3x10mL). The organic extracts were collected, dried over anhydrous sodium sulfate, filtered, and concentrated in *vacuo* to remove solvent. The product was purified by column chromatography on silica gel (100-200 mesh) with EtOAc/hexane system. Finally, the product was recrystallized from acetone/hexane.

$R_f = 0.63$ (20% AcOEt/Hexane), m.p. = 103-105 °C. IR (neat) ν/cm^{-1} : 3018, 2960, 1650, 1593, 1324, 745.

^1H RMN (500 MHz, CDCl_3): δ 6.37 (s, 2H), 4.20 (bs, 1H), 3.29 (bs, 2H), 2.18 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 145.2, 139.4, 124.4, 115.9, 16.2.

4-(2-hydroxyethyl)-2-nitrophenol (**52**)¹⁶



86 mg of this compound were prepared according to the general procedure A in 94% of yield as yellow solid, by using the 4-(2-hydroxyethyl)phenol as starting material.

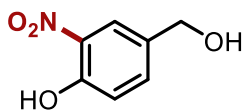
$R_f = 0.69$ (10% AcOEt/Hexane). m.p. = 57-58 °C. IR (neat) ν/cm^{-1} : 3300, 2929, 2847, 1586, 1326, 1179, 836.

^1H RMN (500 MHz, CDCl_3): δ 10.47 (s, 1H), 7.98 (d, $J = 2.2$ Hz, 1H), 7.48 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.11 (d, $J = 8.6$ Hz, 1H), 3.88 (t, $J = 6.4$ Hz, 2H), 2.86 (t, $J = 6.4$ Hz, 2H), 1.51 (bs, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 153.9, 138.7, 131.4, 124.8, 120.1, 115.6, 63.2, 37.8.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_4$ [M-H]: 182.0459, found 182.0447.

4-(hydroxymethyl)-2-nitrophenol (**53**)¹⁷



62 mg of this compound was prepared according to the general procedure A in 73% of yield as yellow solid, by using the 4-(2-hydroxymethyl)phenol as starting material.

¹⁶ Schuhmann I., Fotso-Fondja Yao C. B., Al-Zereini W., Anke H., Helmke E. and Laatsch H. *The Journal of Antibiotics*, **2009**, 62, 453–460.

¹⁷ Sviridov, S.I. & Ermolinskii, B.S. *Chem Nat Compd*, **1990**, 26, 691-696.

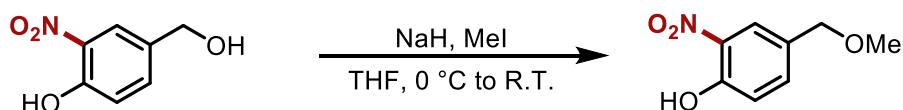
$R_f = 0.51$ (10% AcOEt/Hexane). m.p. = 95-96 °C. IR (neat) ν/cm^{-1} : 3293, 2912, 2832, 1591, 1324, 1195, 883.

^1H RMN (500 MHz, CDCl_3): δ 10.55 (s, 1H), 8.32 – 7.97 (m, 1H), 7.60 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.16 (d, $J = 8.6$ Hz, 1H), 4.69 (d, $J = 5.7$ Hz, 2H), 1.83 (t, $J = 5.7$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) 154.6, 136.5, 133.5, 133.4, 123.2, 120.4, 63.8.

HRMS (ESI-) calcd. for $\text{C}_7\text{H}_6\text{NO}_4$ [M-H]: 168.0302, found 168.0294.

4-(methoxymethyl)-2-nitrophenol (**54**)¹⁷



The following compound was obtained by using 4-(2-methoxymethyl)phenol in 28% yield as 25 mg of yellow oil. In a round-bottom flask the nitro compound **52** (0.07 mmol) was dissolved and cooled at 0 °C. NaH (2.1 equiv) was slowly added to the mixture and stirred. MeI (1.05 equiv) was added to the mixture and the reaction was carried out to room temperature and monitored by TLC until **52** was finished. The reaction was stopped by adding brine. Was extracted with ethyl acetate (3x10mL). The organic extracts were collected, dried over anhydrous sodium sulfate, filtered, and concentrated in *vacuo* to remove solvent. The product was purified by PLC with EtOAc/hexane system.

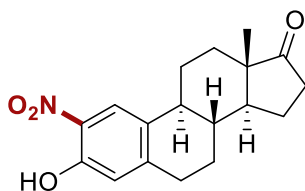
$R_f = 0.67$ (10% AcOEt/Hexane), 168-171 °C. IR (neat) ν/cm^{-1} : 3112, 2966, 2857, 1594, 1315, 1177, 861.

^1H RMN (500 MHz, CDCl_3): δ 10.57 (s, 1H), 8.08 (d, $J = 1.4$ Hz, 1H), 7.57 (dd, $J = 8.7, 1.9$ Hz, 1H), 7.15 (d, $J = 8.6$ Hz, 1H), 4.42 (s, 2H), 3.41 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 154.7, 137.1, 131.0, 129.5, 124.0, 120.3, 73.2, 58.5.

HRMS (ESI-) calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$ [M-H]: 182.0459, found 182.0448.

(8R,9S,13S,14S)-3-hydroxy-13-methyl-2-nitro-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (**55**)



41 mg of this compound were prepared according to the general procedure A in 26% of yield as yellow solid, by using the estrone as starting material.

$R_f = 0.62$, m.p: 179-181° C, IR (neat) ν/cm^{-1} : 3312, 1728, 1502, 1299.

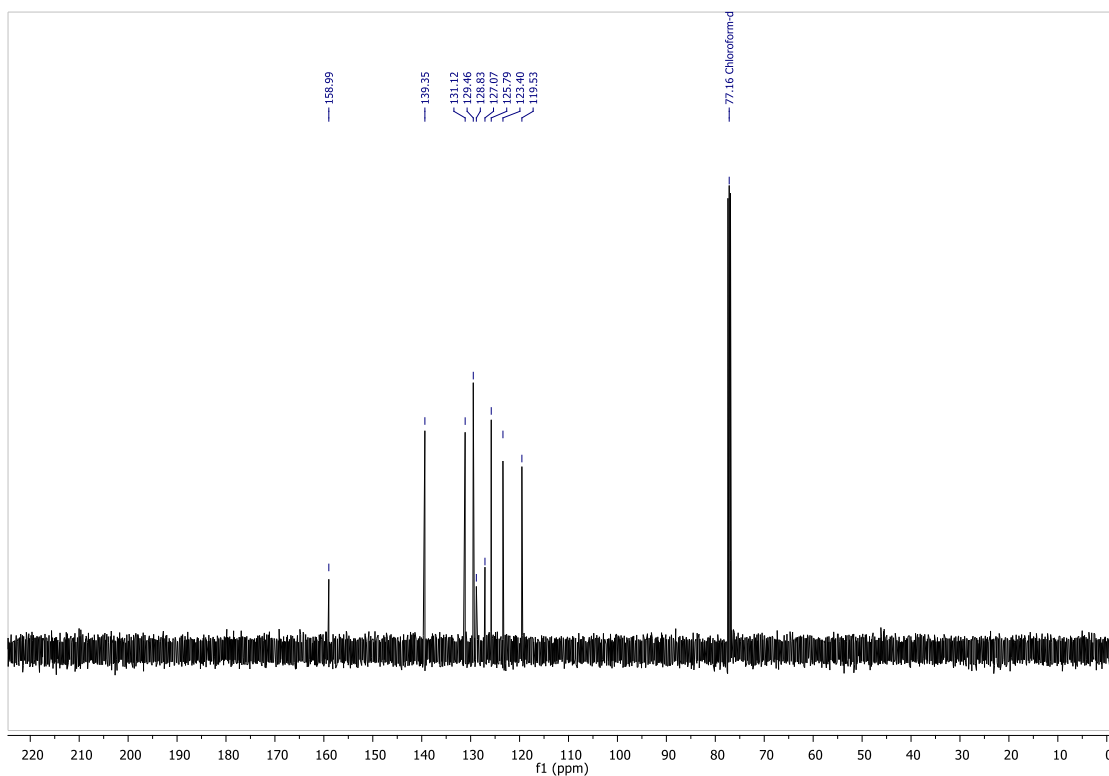
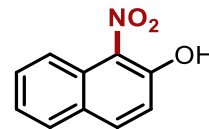
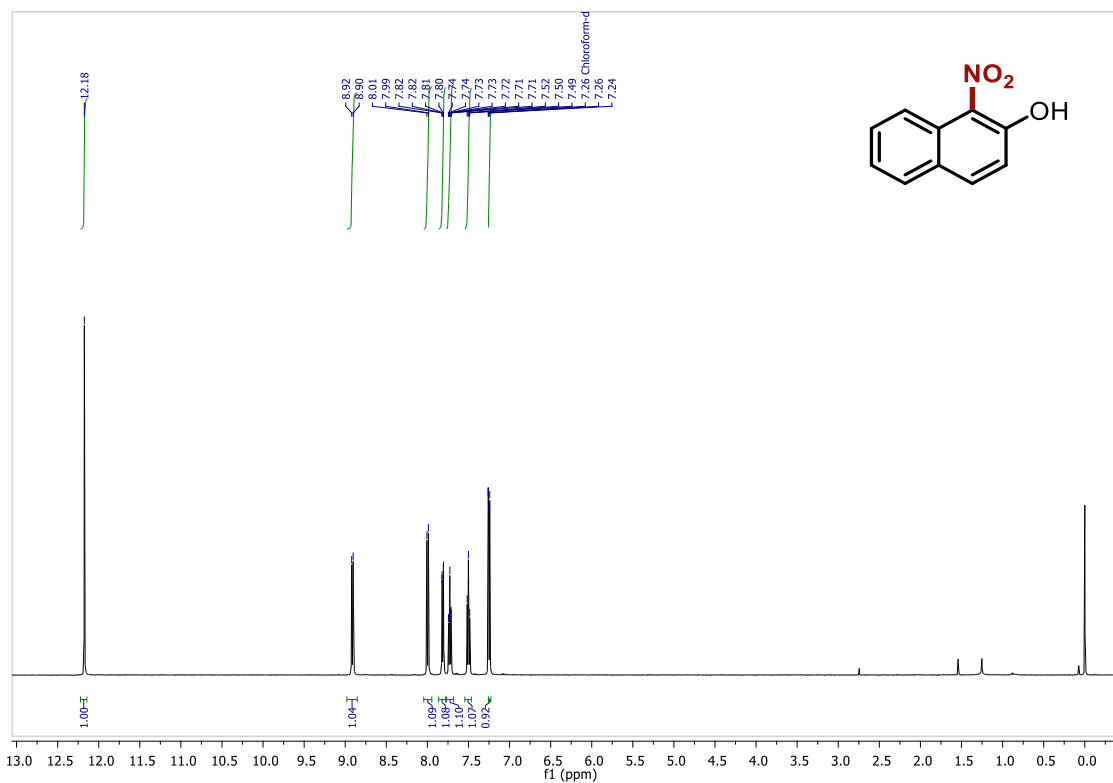
^1H RMN (400 MHz, Acetone- d_6) δ 10.28 (s, 1H), 7.98 (s, 1H), 6.92 (s, 1H), 3.04 – 2.92 (m, 2H), 2.86 (s, 1H), 2.51 – 2.38 (m, 2H), 2.36 – 2.23 (m, 1H), 2.14 – 2.08 (m, 2H), 1.74 – 1.41 (m, 6H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, Acetone- d_6) δ 161.7, 149.8, 134.1, 132.8, 122.2, 119.7, 51.0, 48.3, 44.2, 38.5, 36.0, 32.3, 30.2, 26.5, 26.4, 22.1, 14.0.

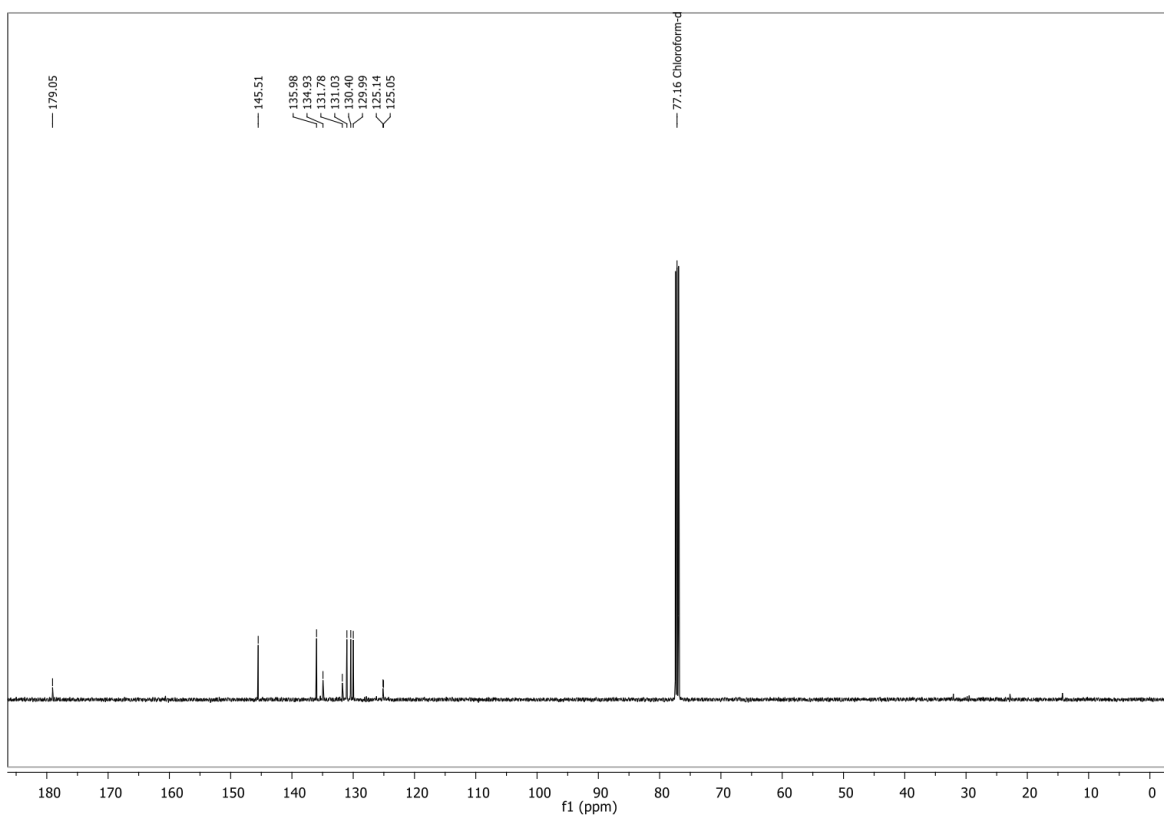
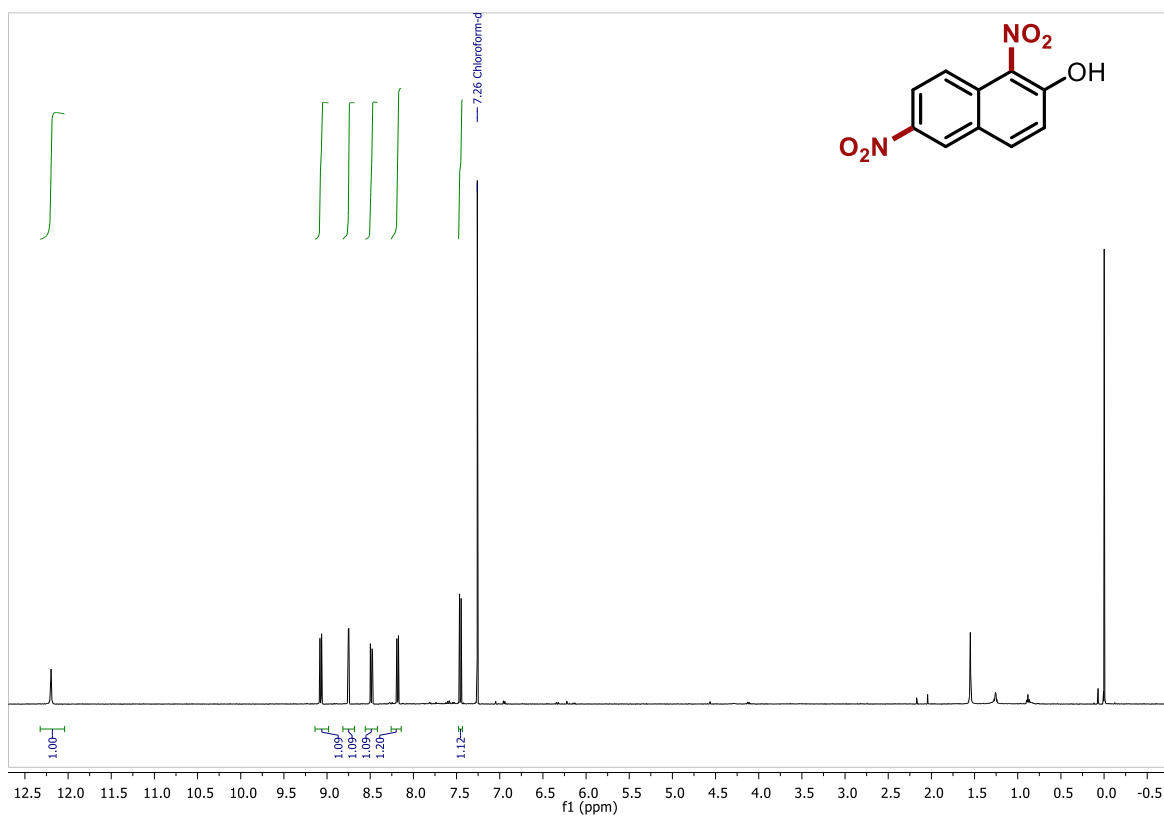
HRMS (ESI-) calcd. for $\text{C}_{18}\text{H}_{20}\text{NO}_4$ [M-H]: 314.1398, found 314.1396.

4. Copies of ^1H and ^{13}C NMR Spectra

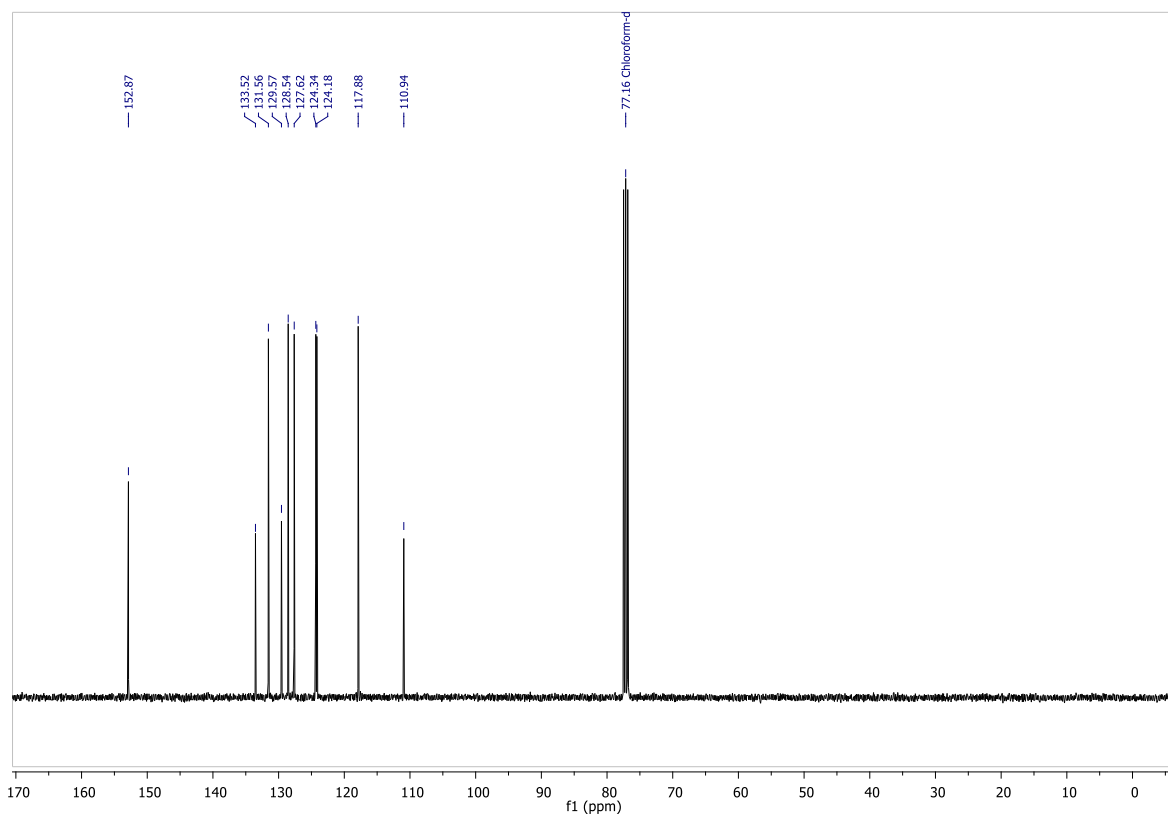
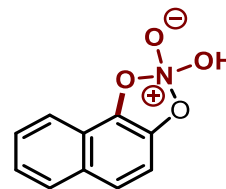
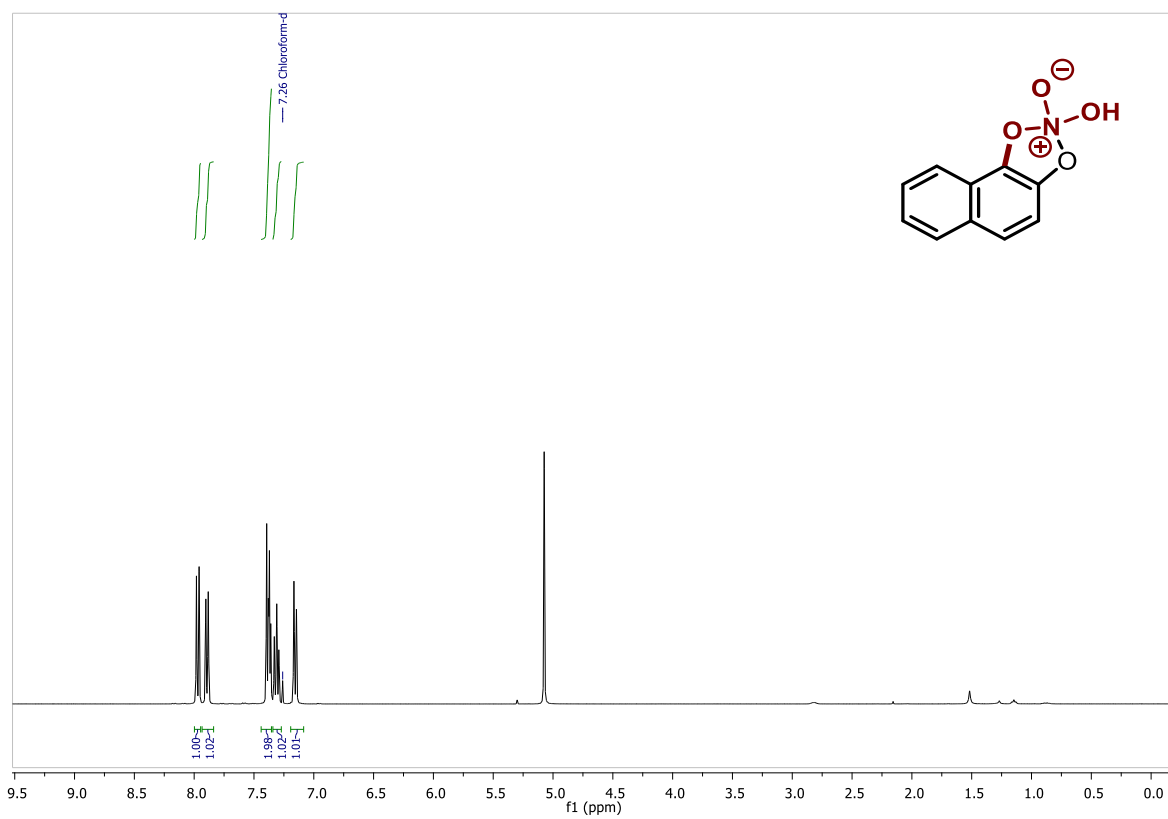
1-nitronaphthalen-2-ol (1)



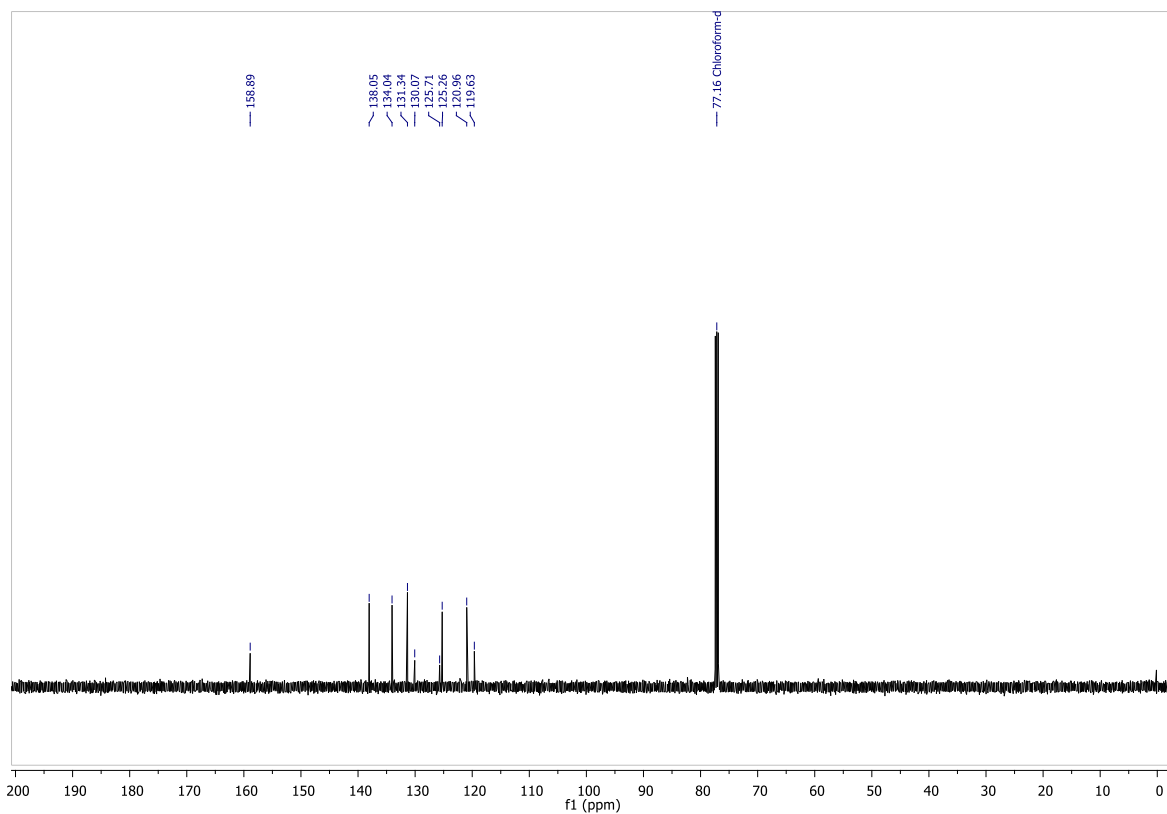
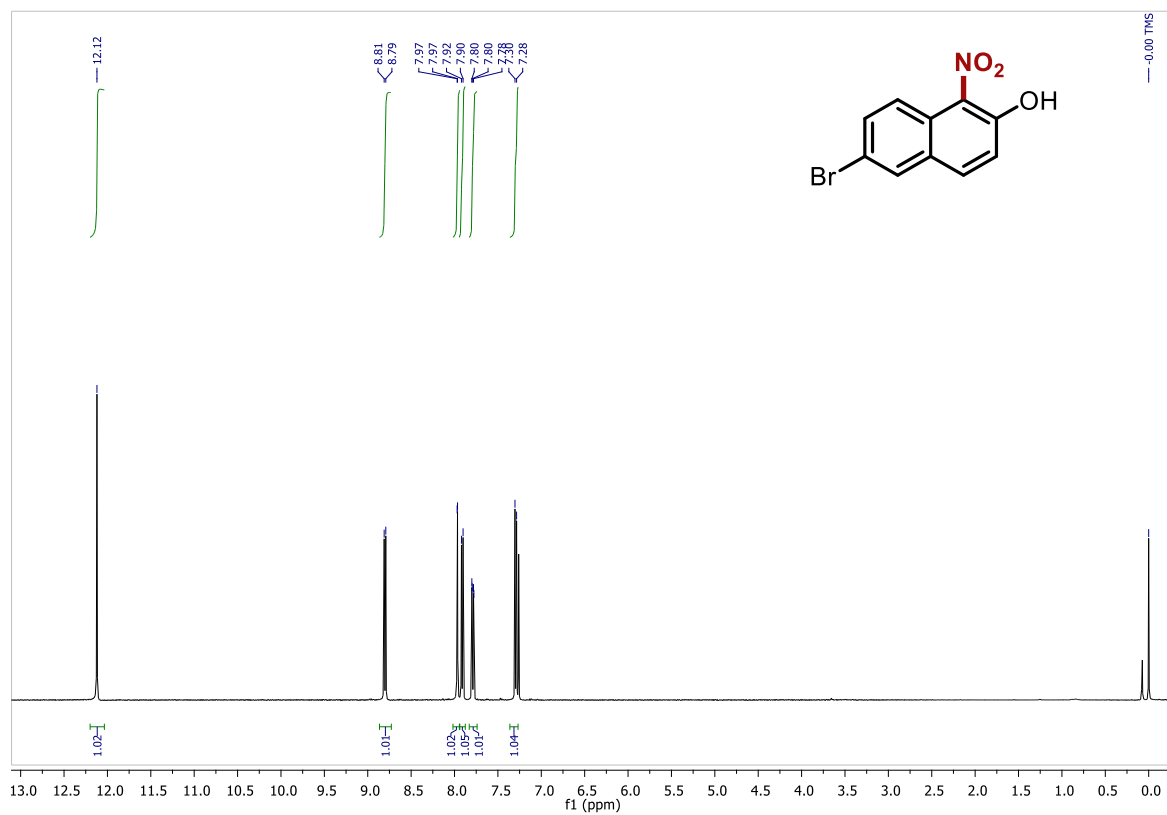
1,6-dinitronaphthalen-2-ol (2)



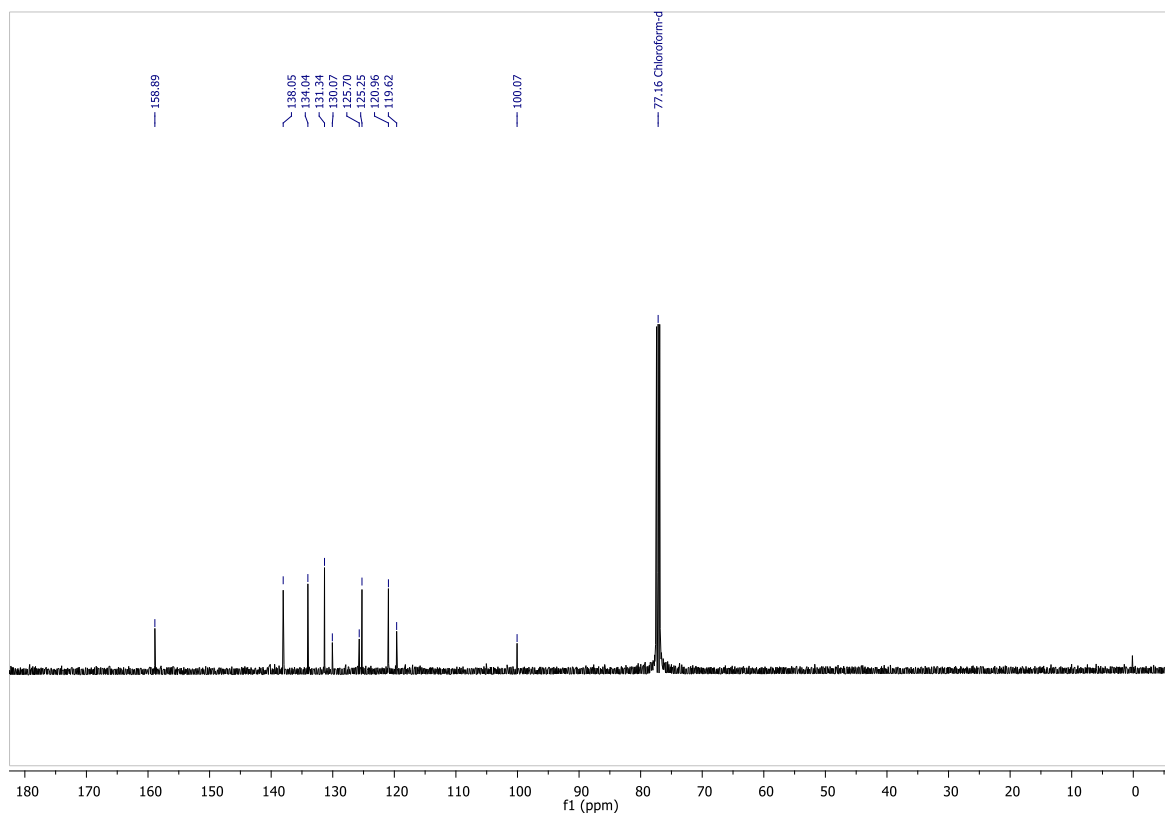
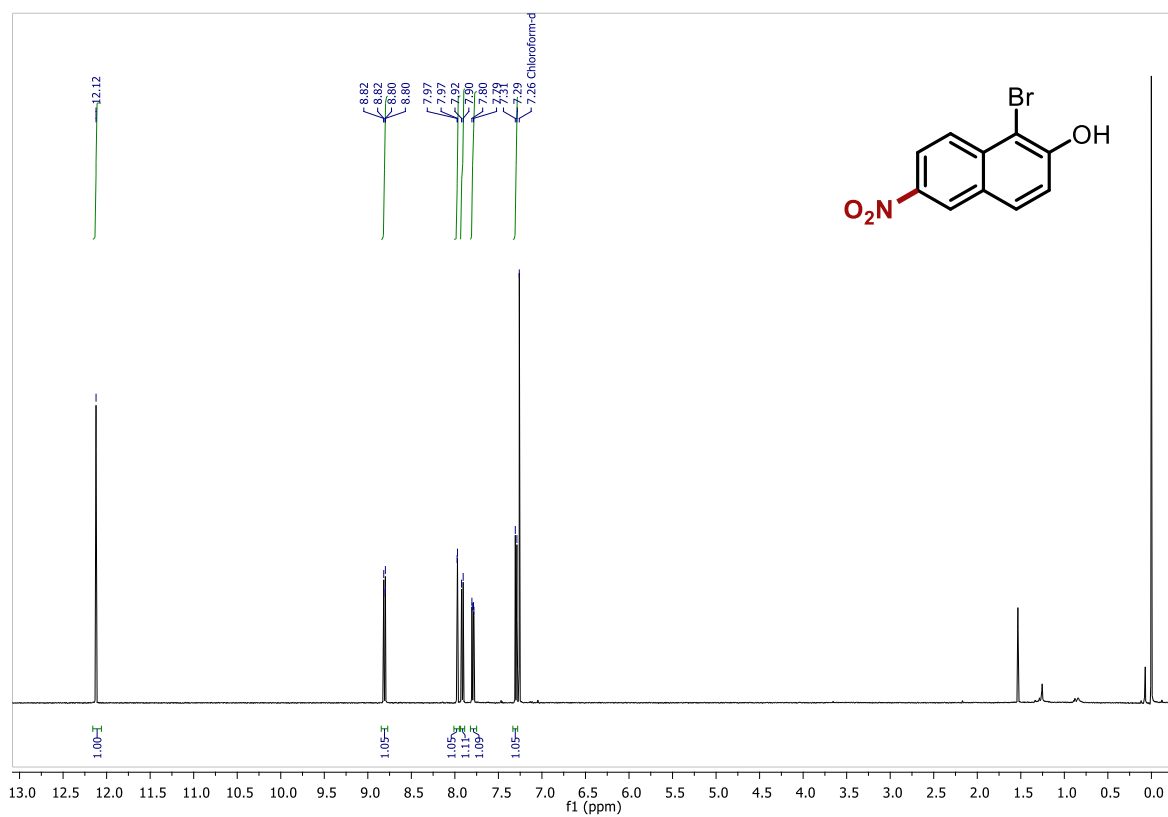
2-hydroxynaphtho[1,2-d][1,3,2]dioxazole 2-oxide (3)



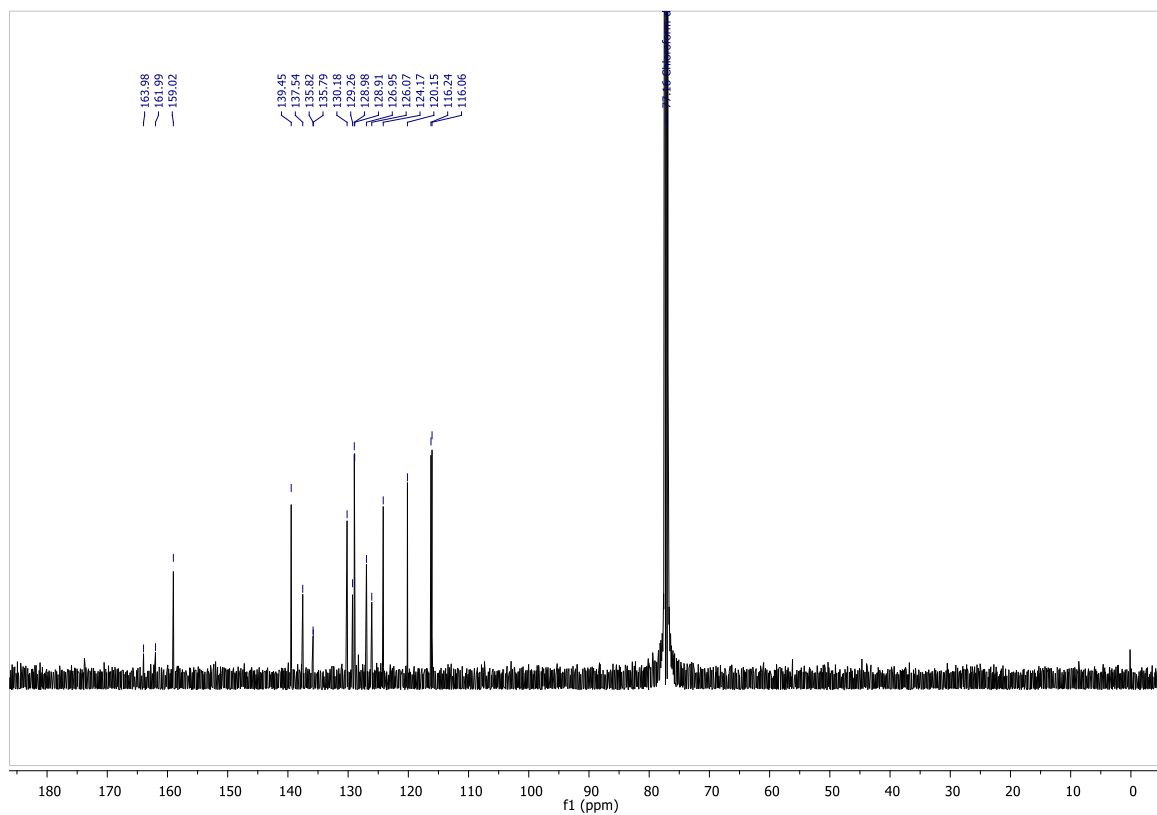
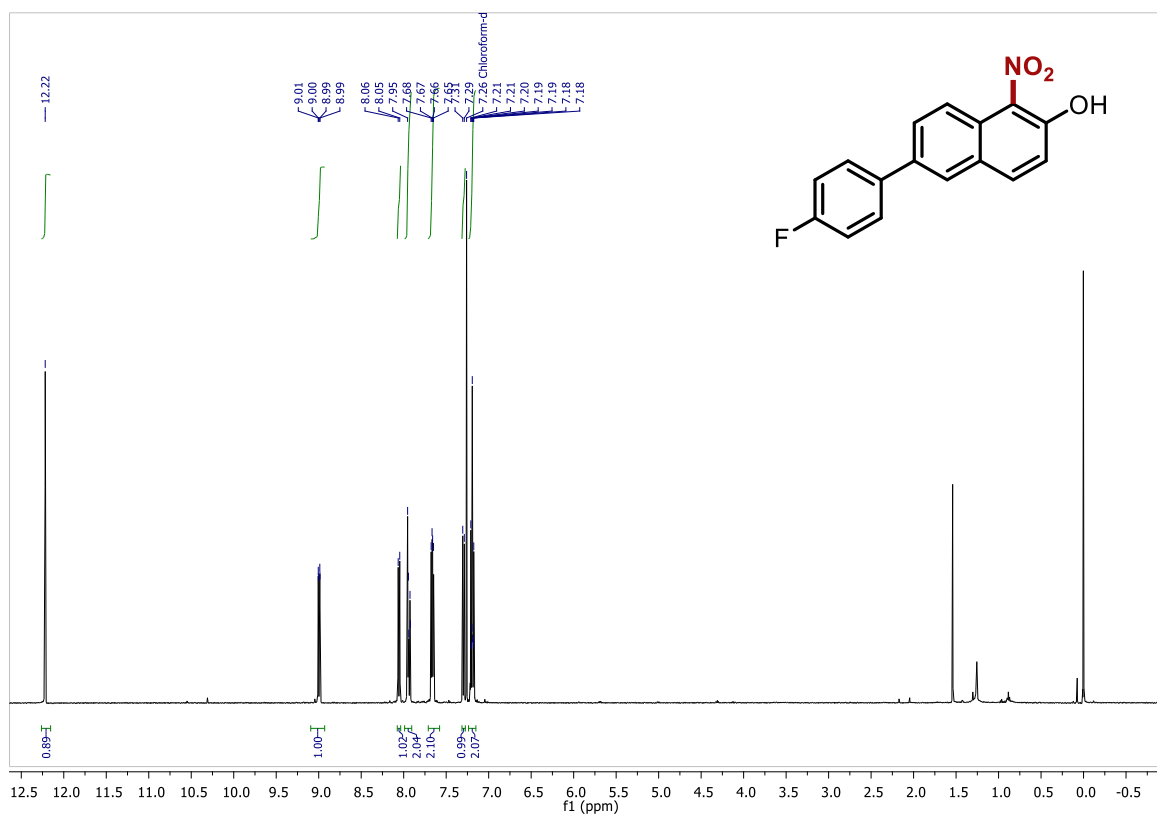
6-bromo-1-nitronaphthalen-2-ol (4)



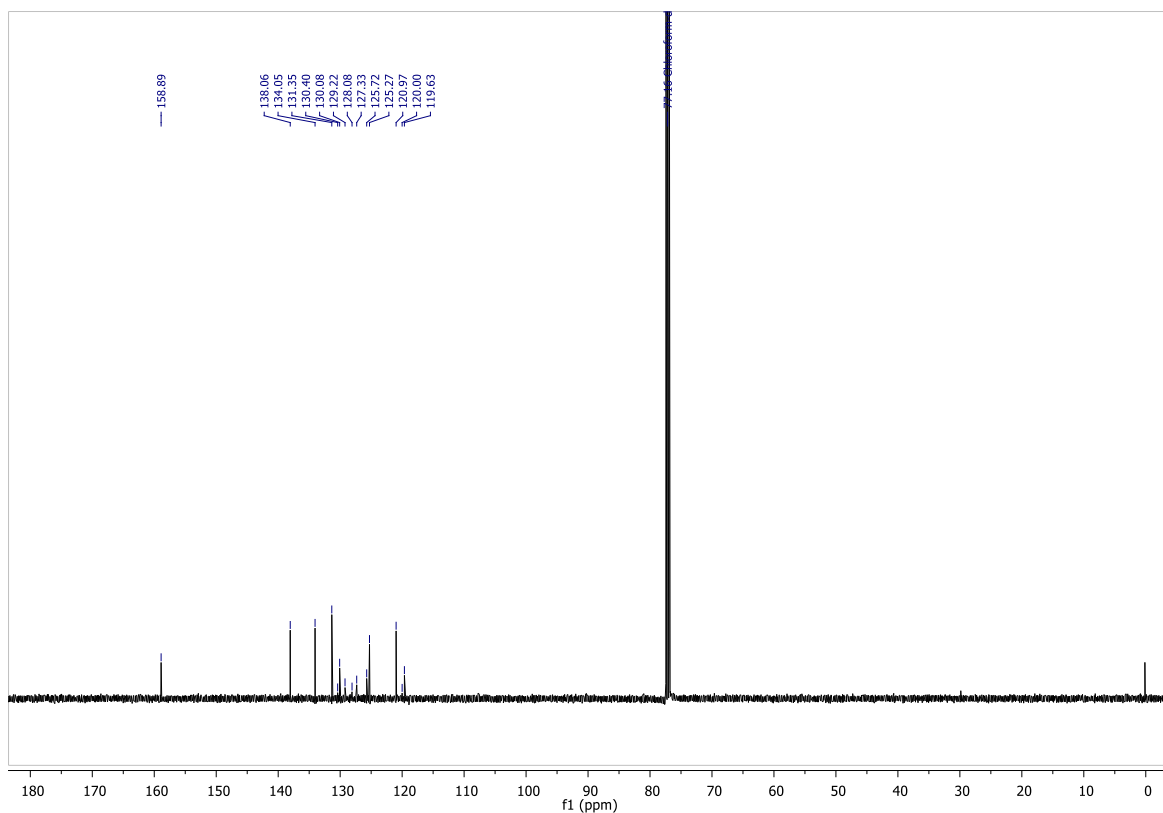
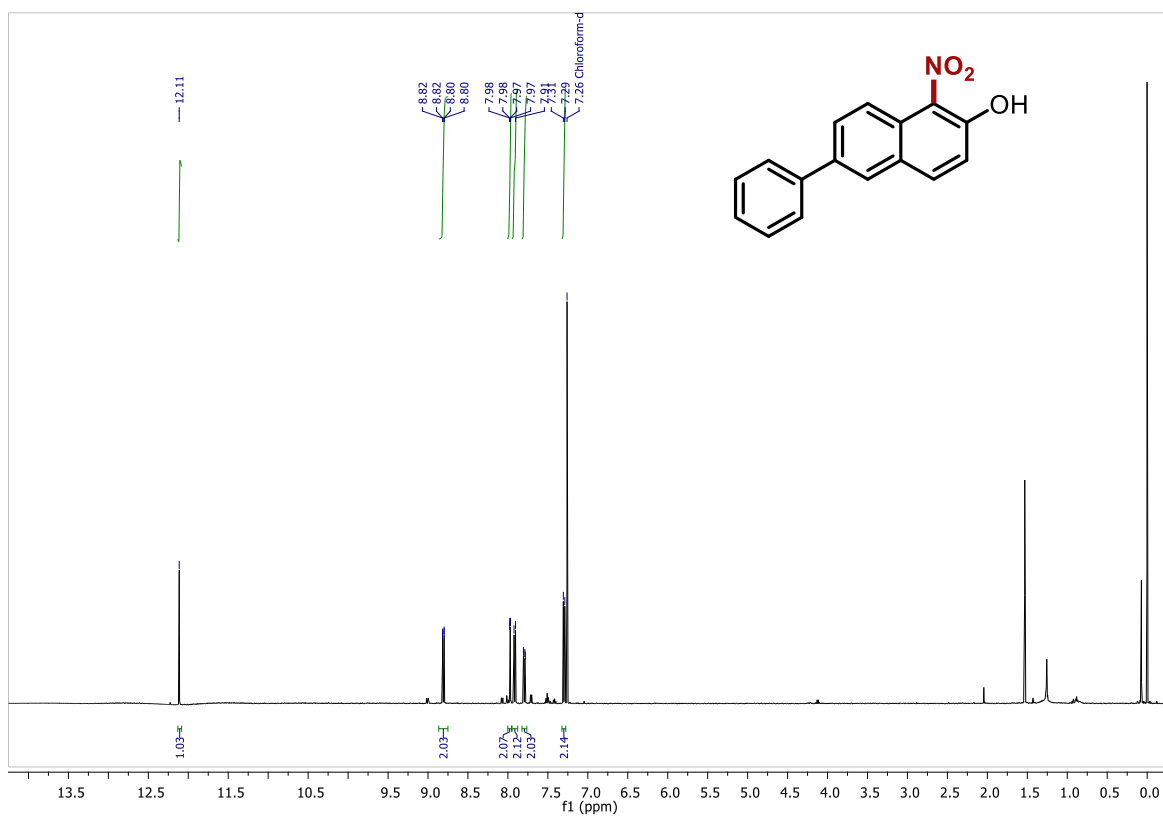
1-bromo-6-nitronaphthalen-2-ol (5)



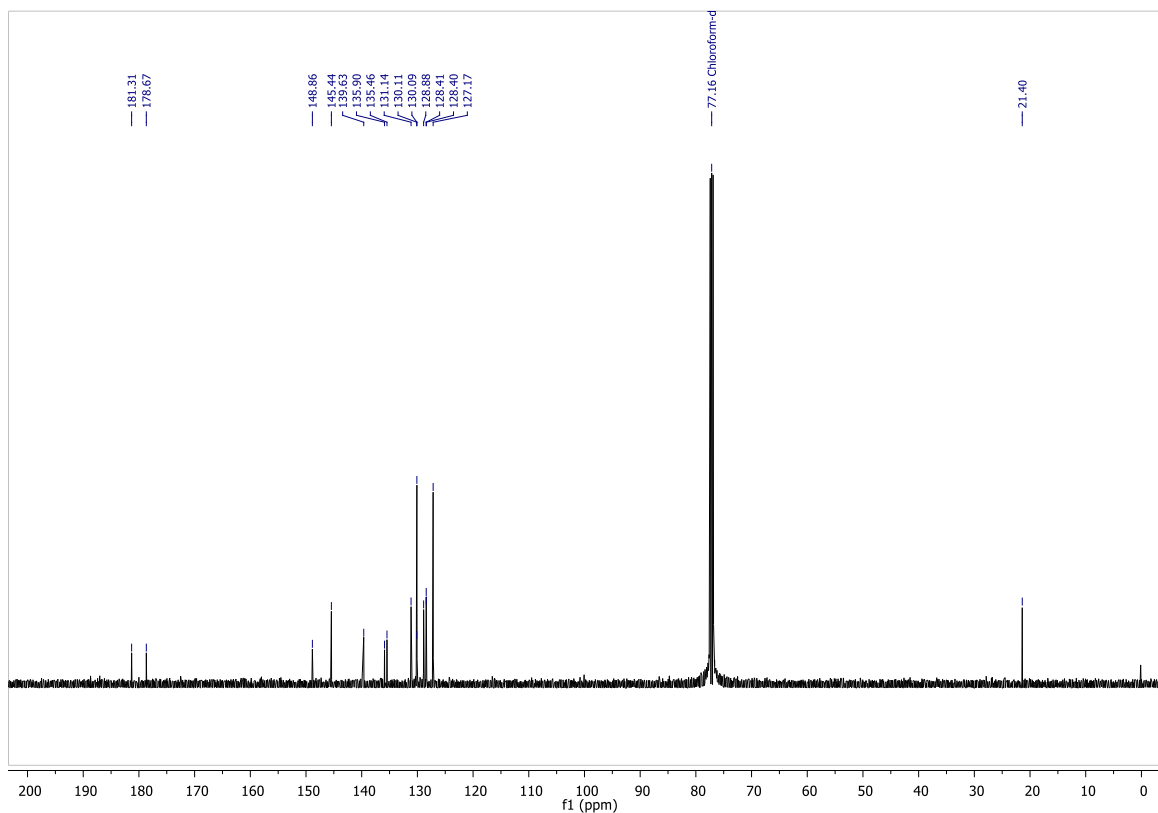
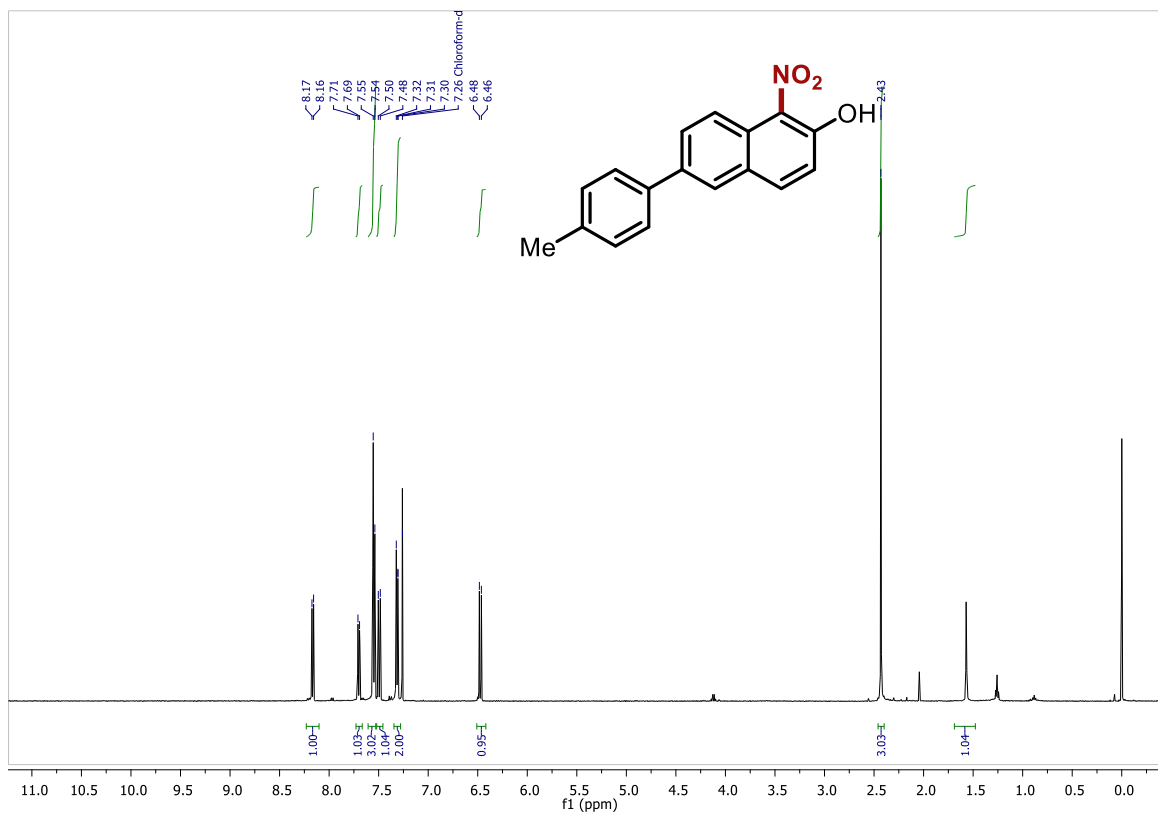
6-(4-fluorophenyl)-1-nitronaphthalen-2-ol (6)



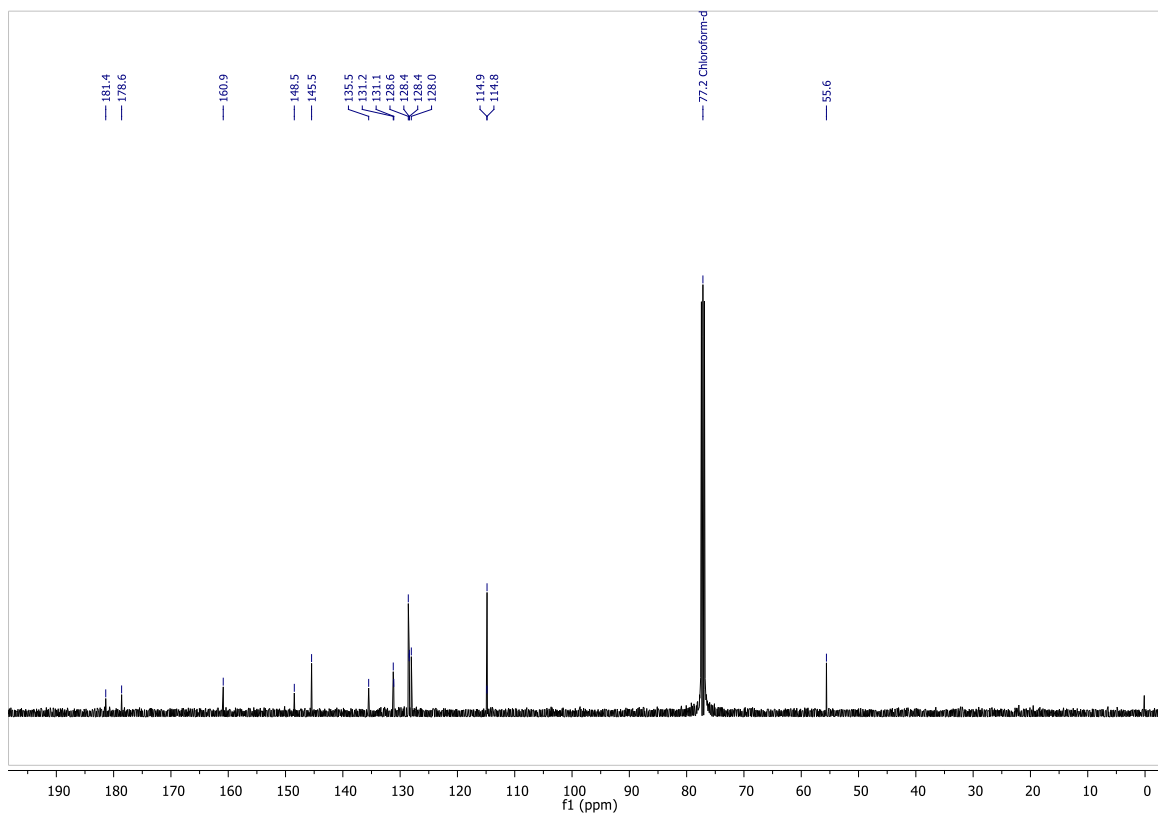
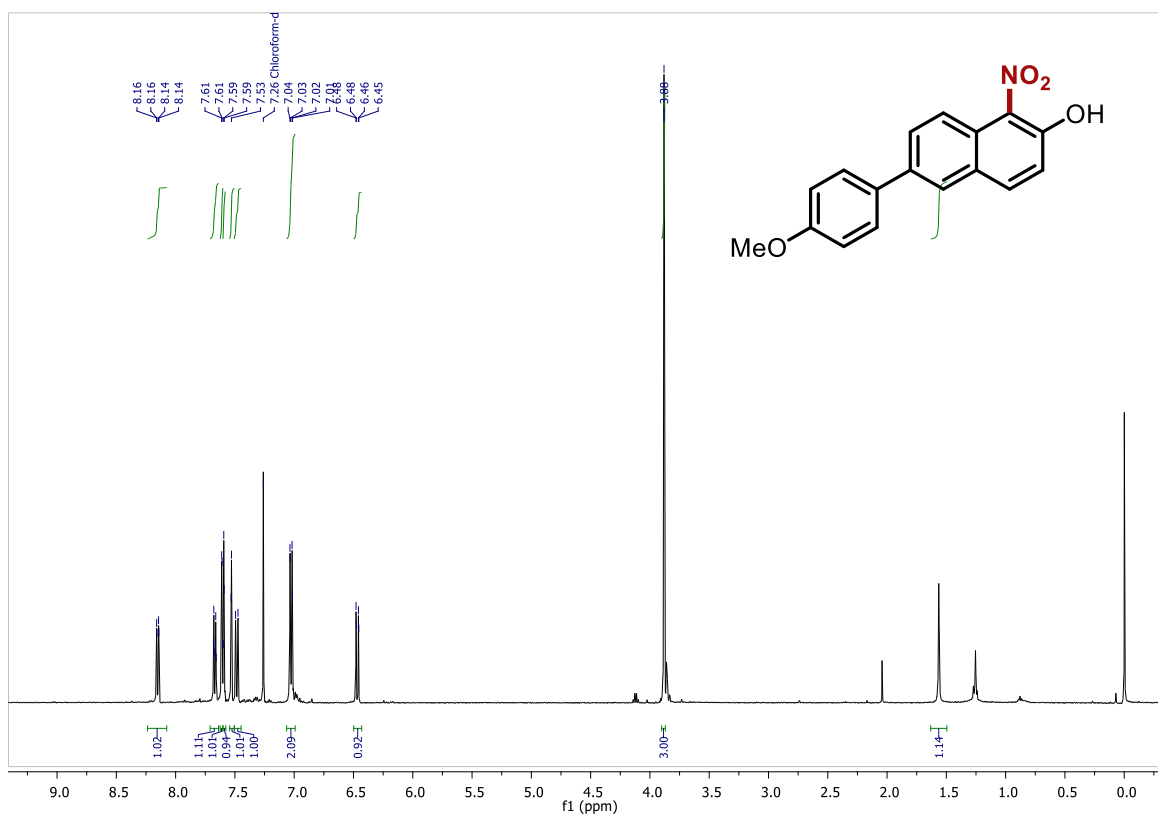
1-nitro-6-phenylnaphthalen-2-ol (7)



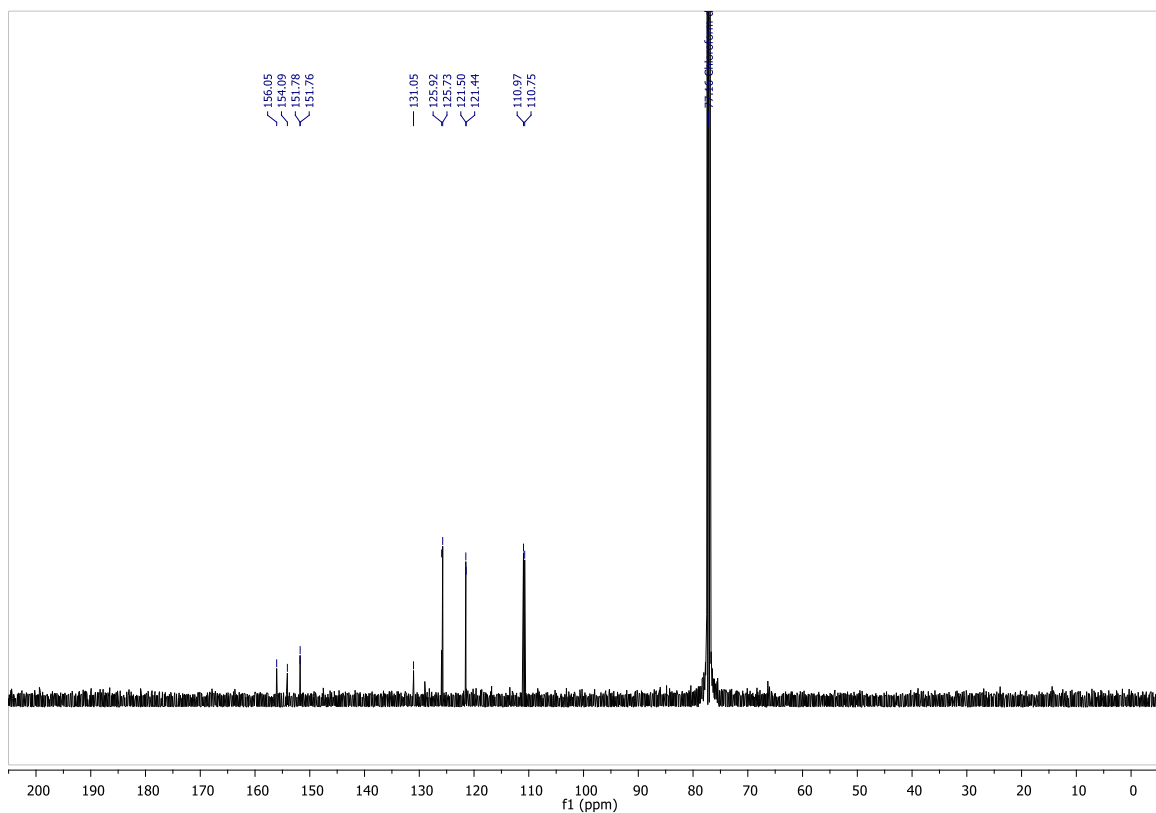
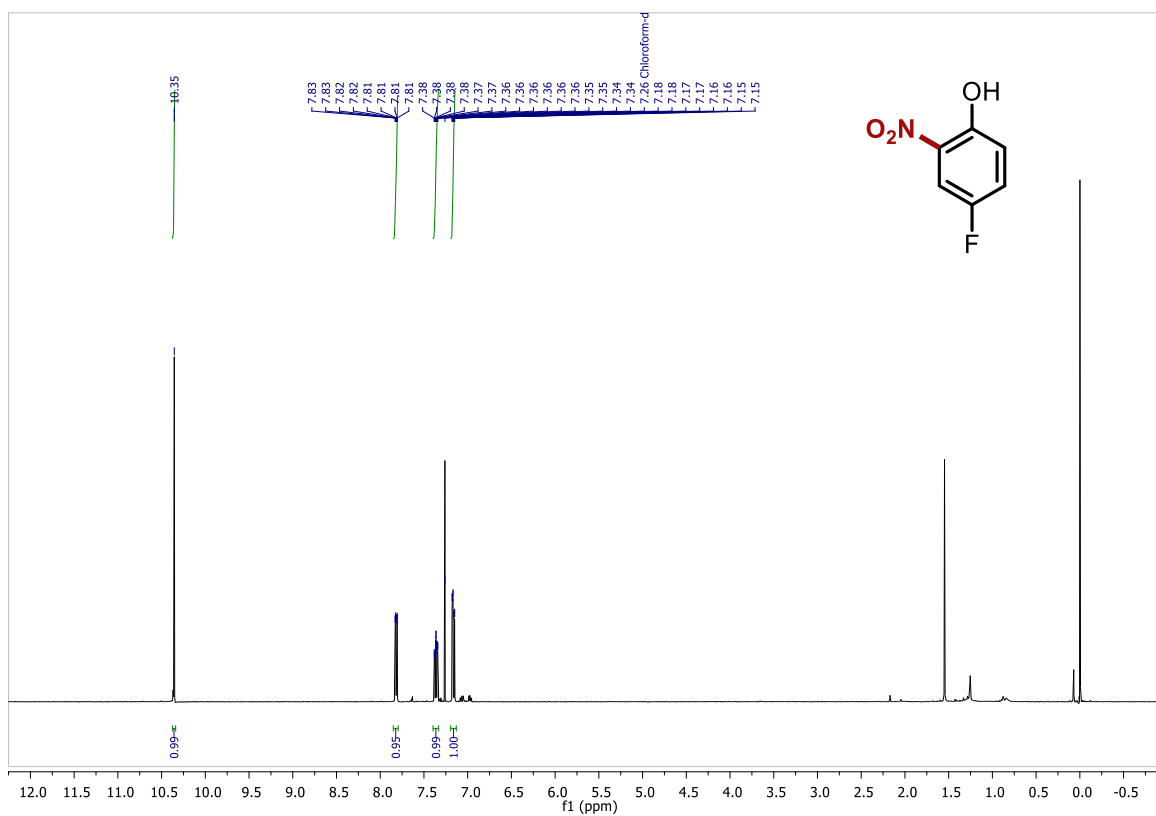
1-nitro-6-(*p*-tolyl)naphthalen-2-ol (8)



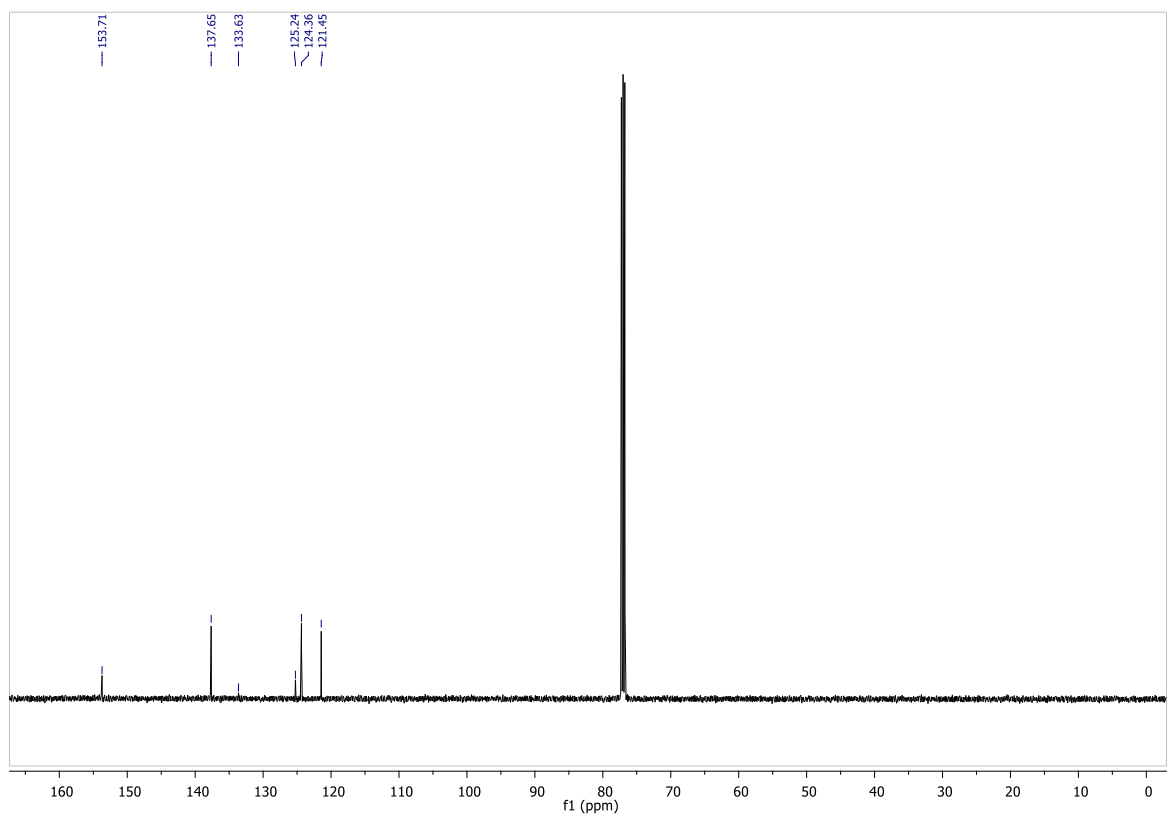
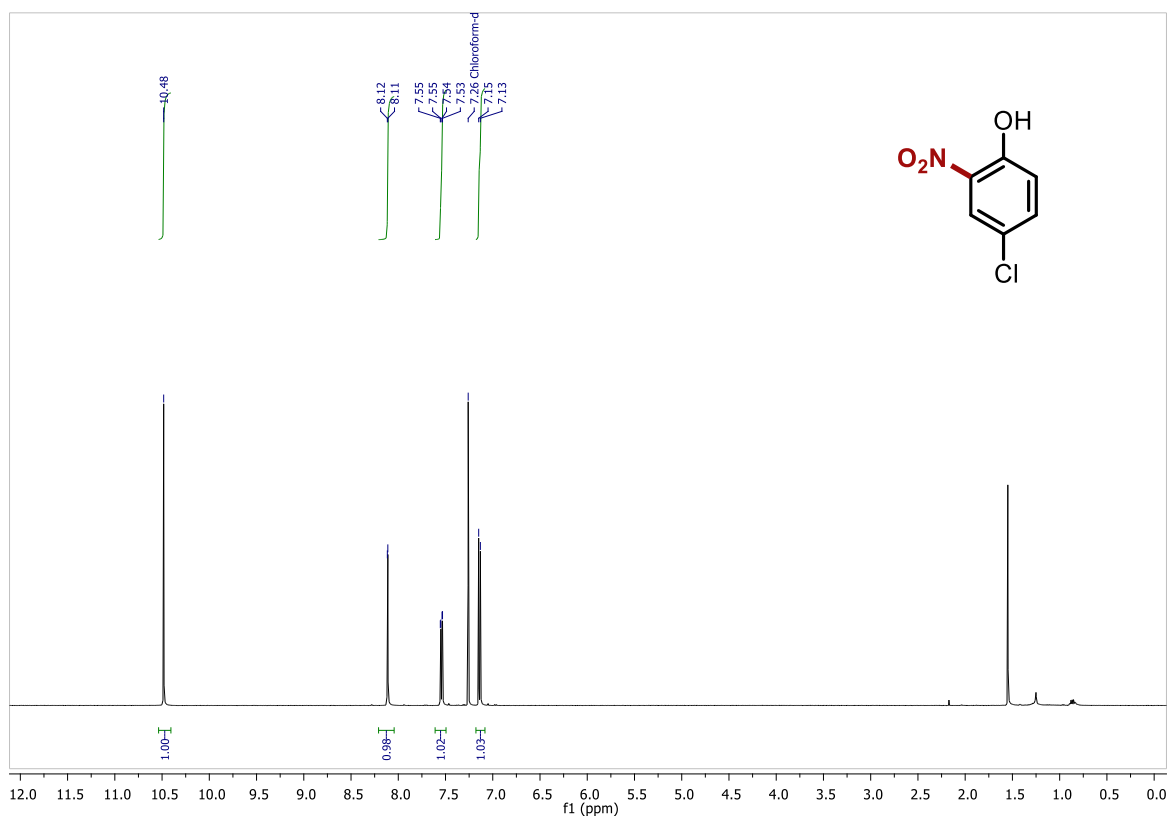
6-(4-methoxyphenyl)-1-nitronaphthalen-2-ol (9)



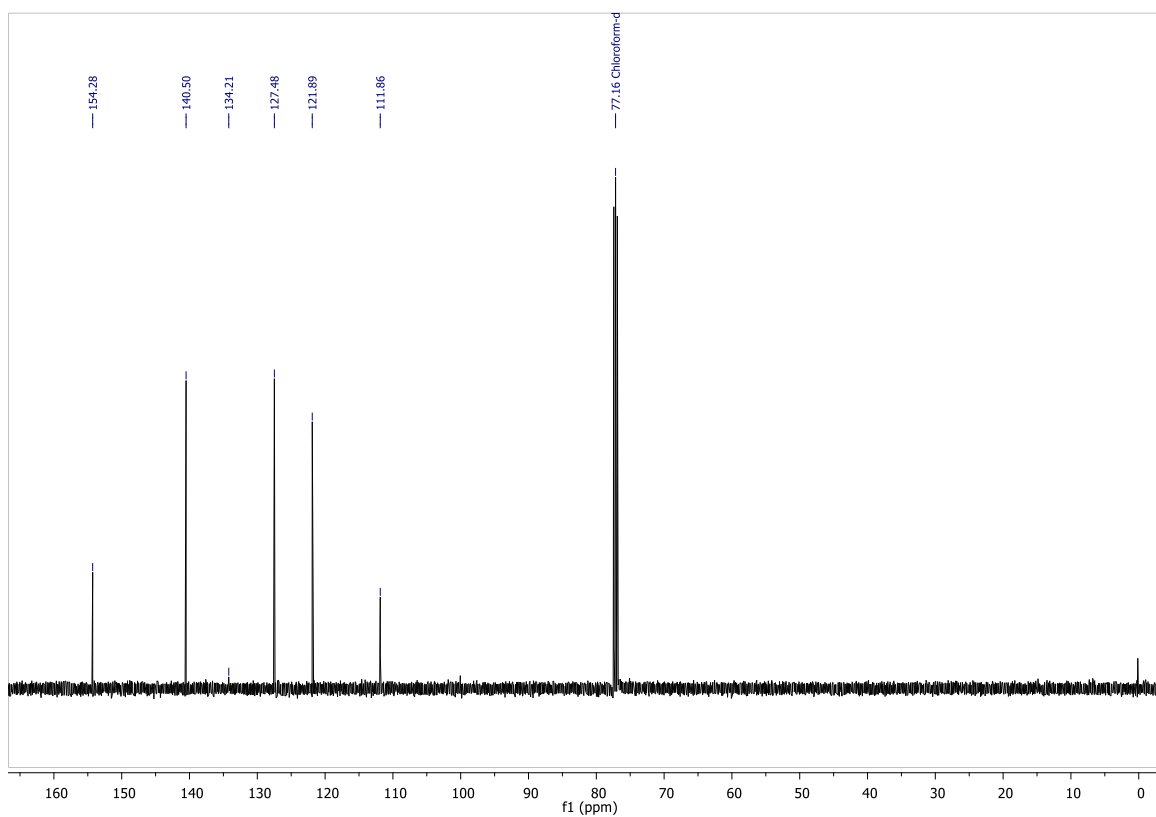
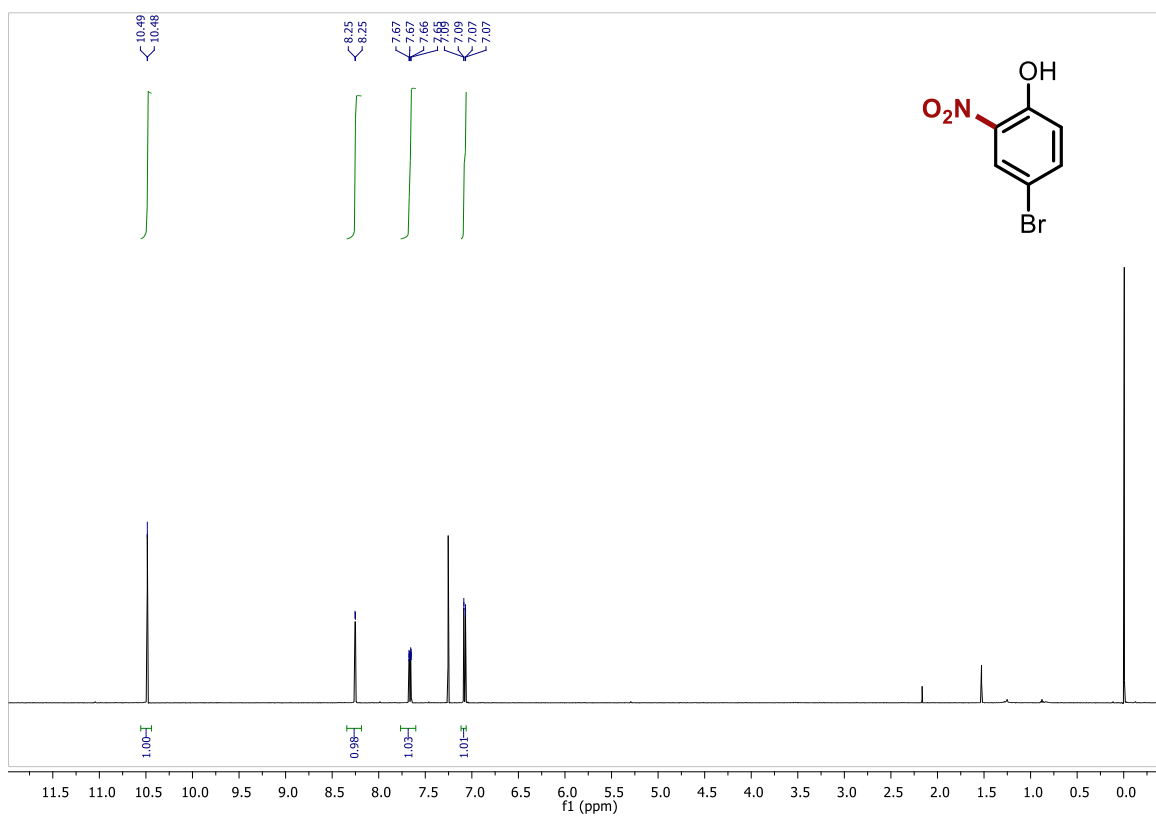
4-fluoro-2-nitrophenol (10)



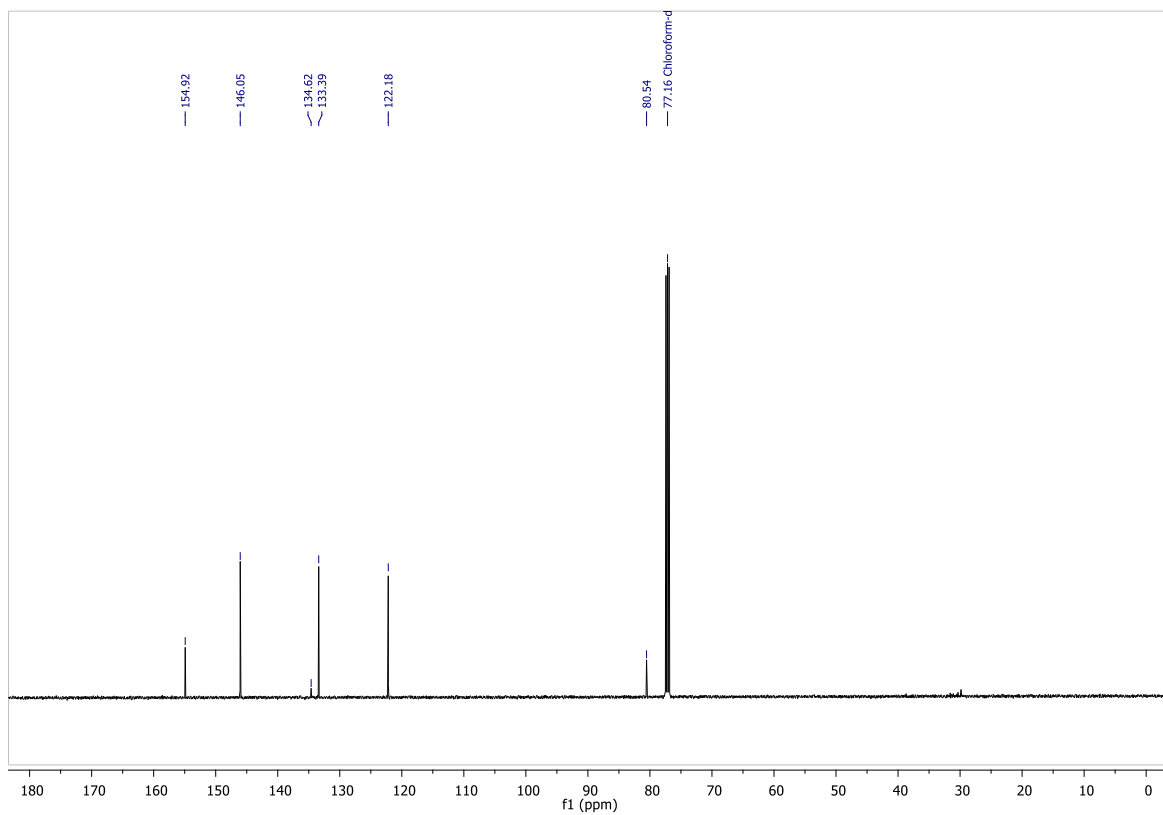
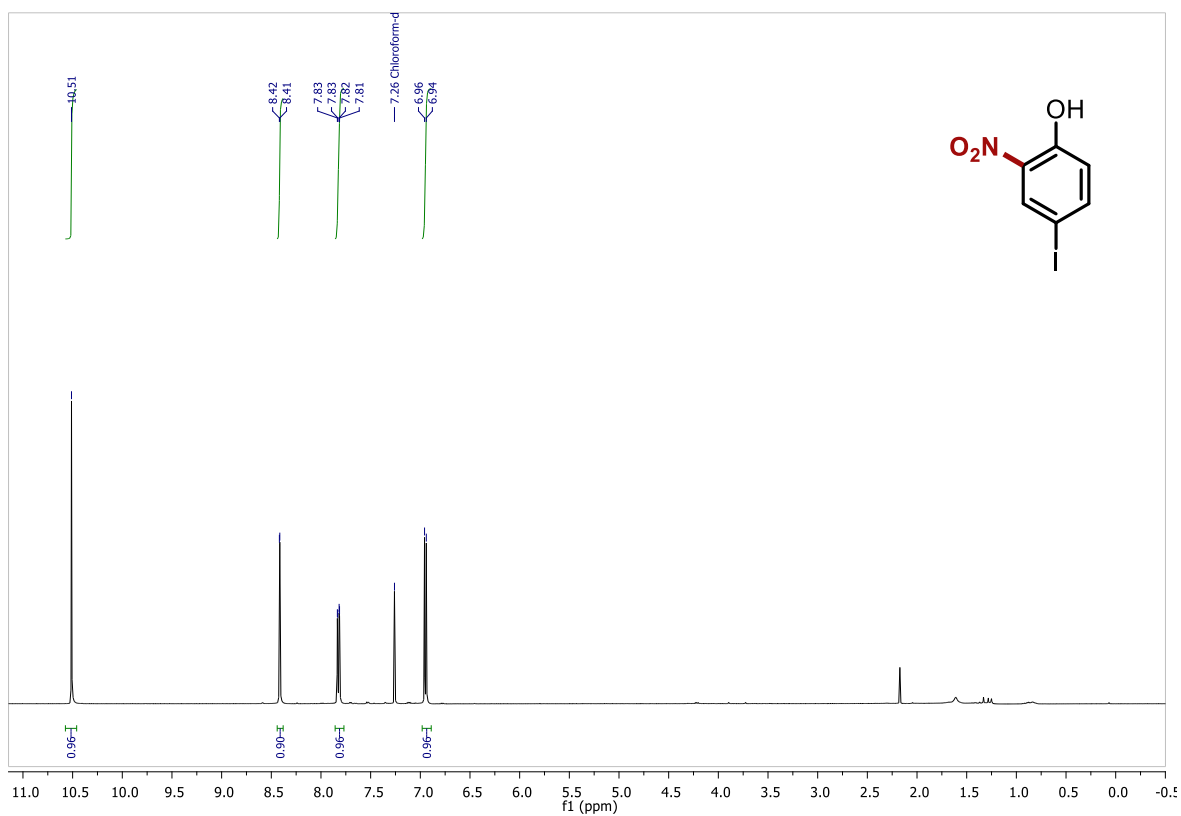
4-chloro-2-nitrophenol (11)



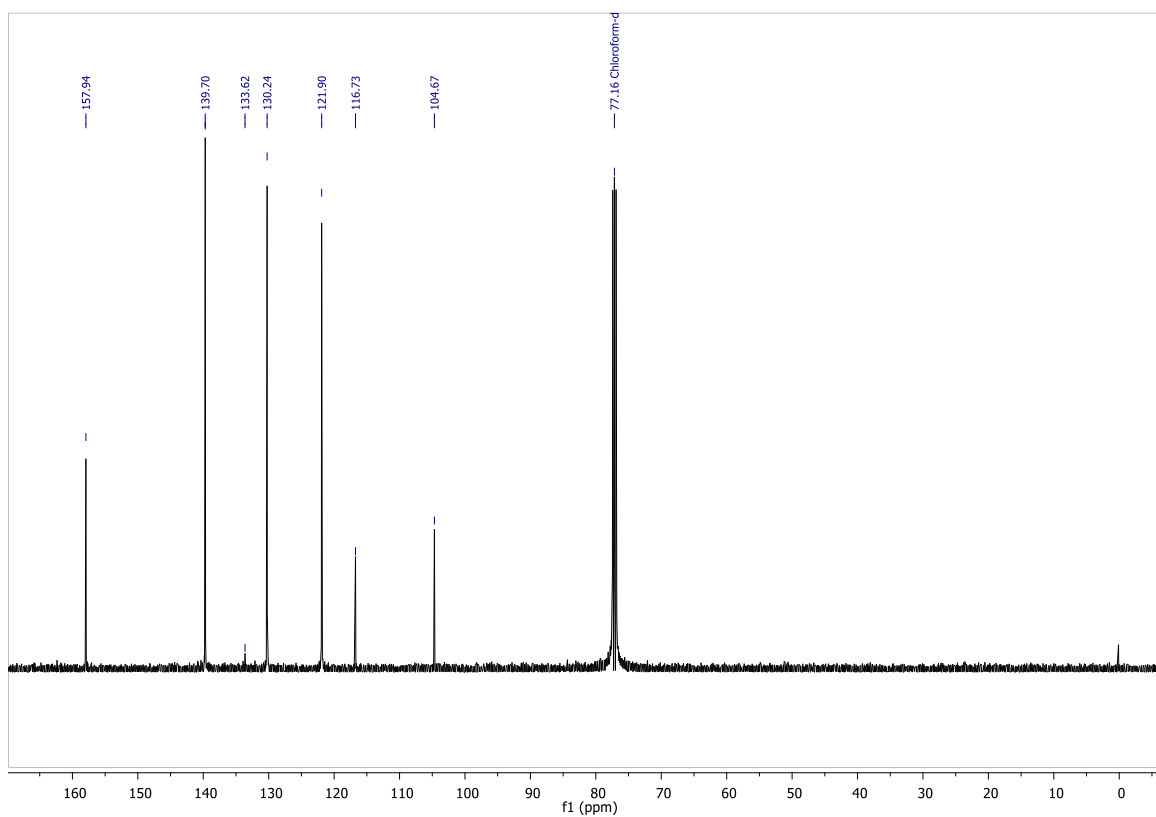
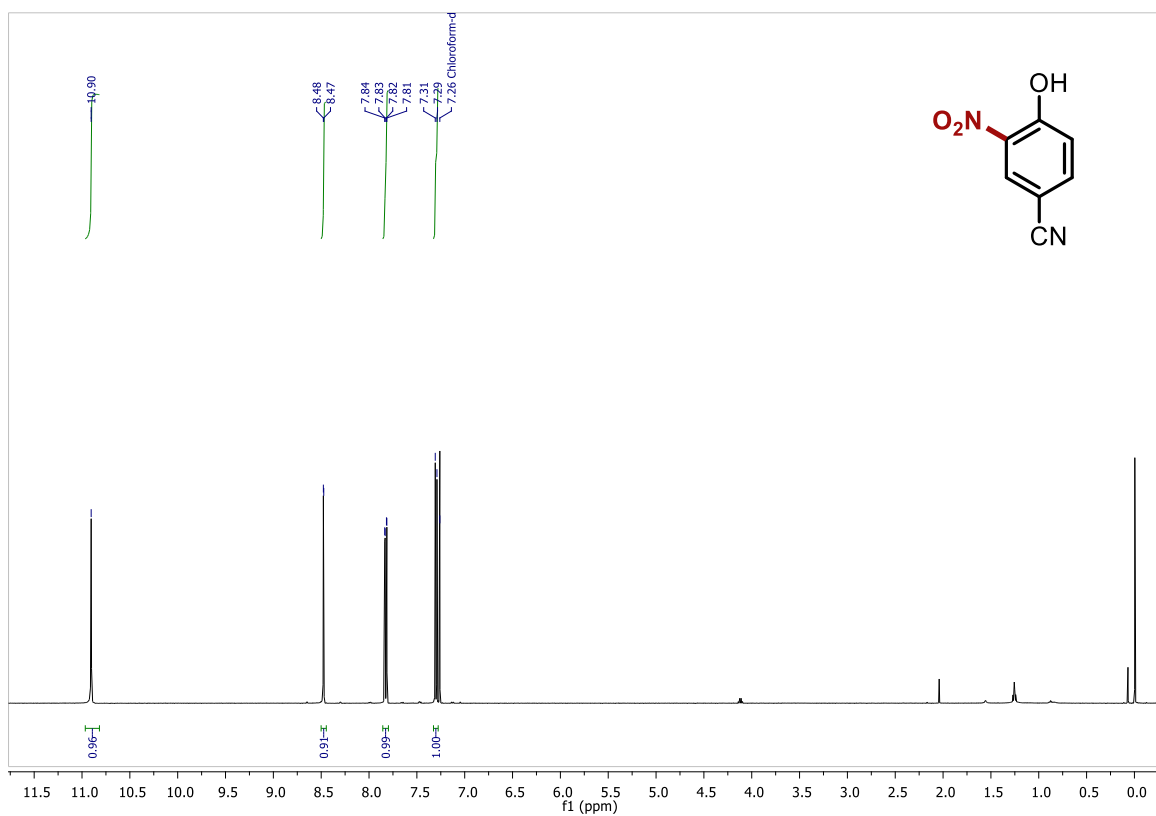
4-bromo-2-nitrophenol (12)



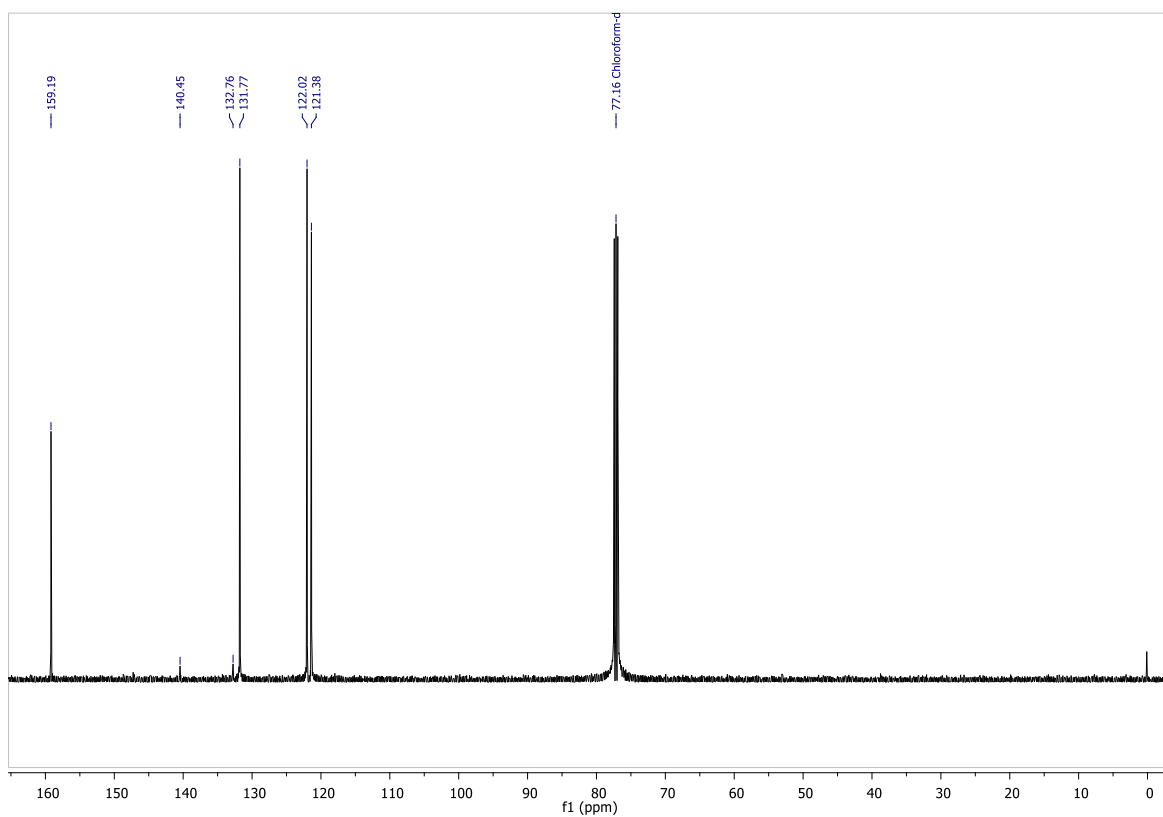
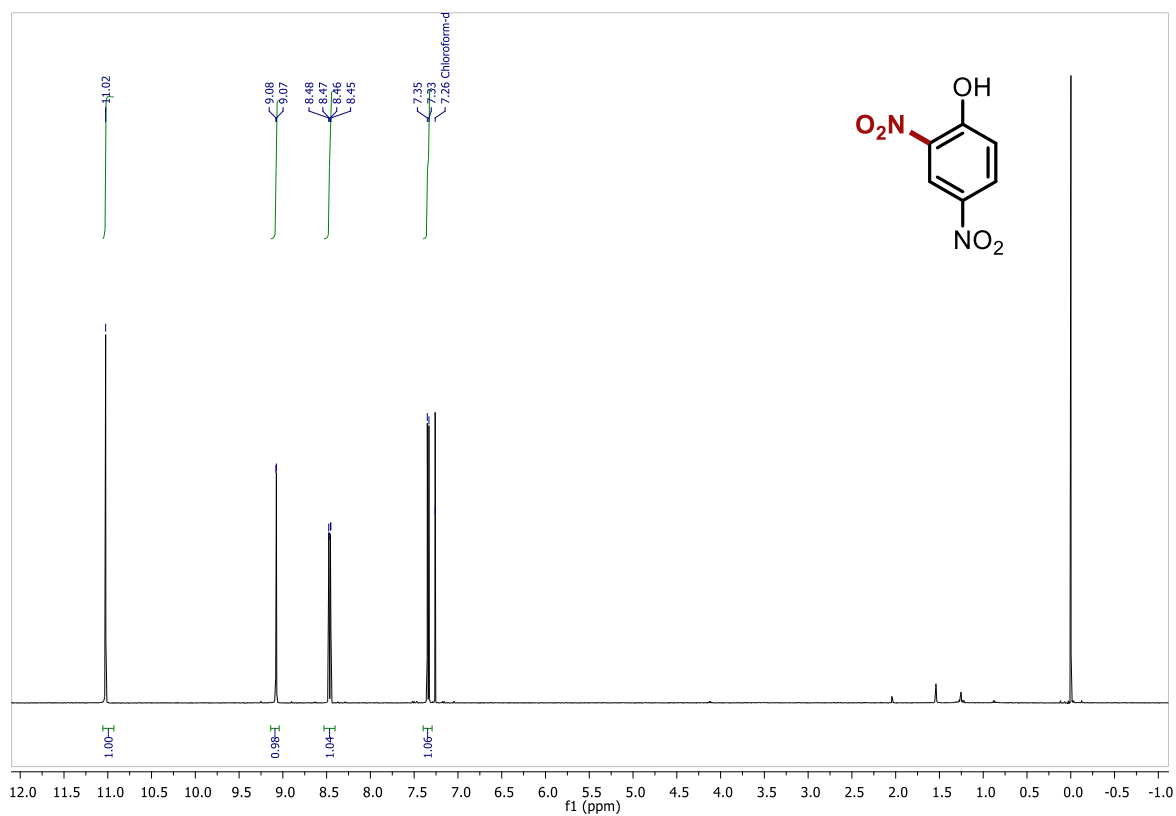
4-iodo-2-nitrophenol (13)



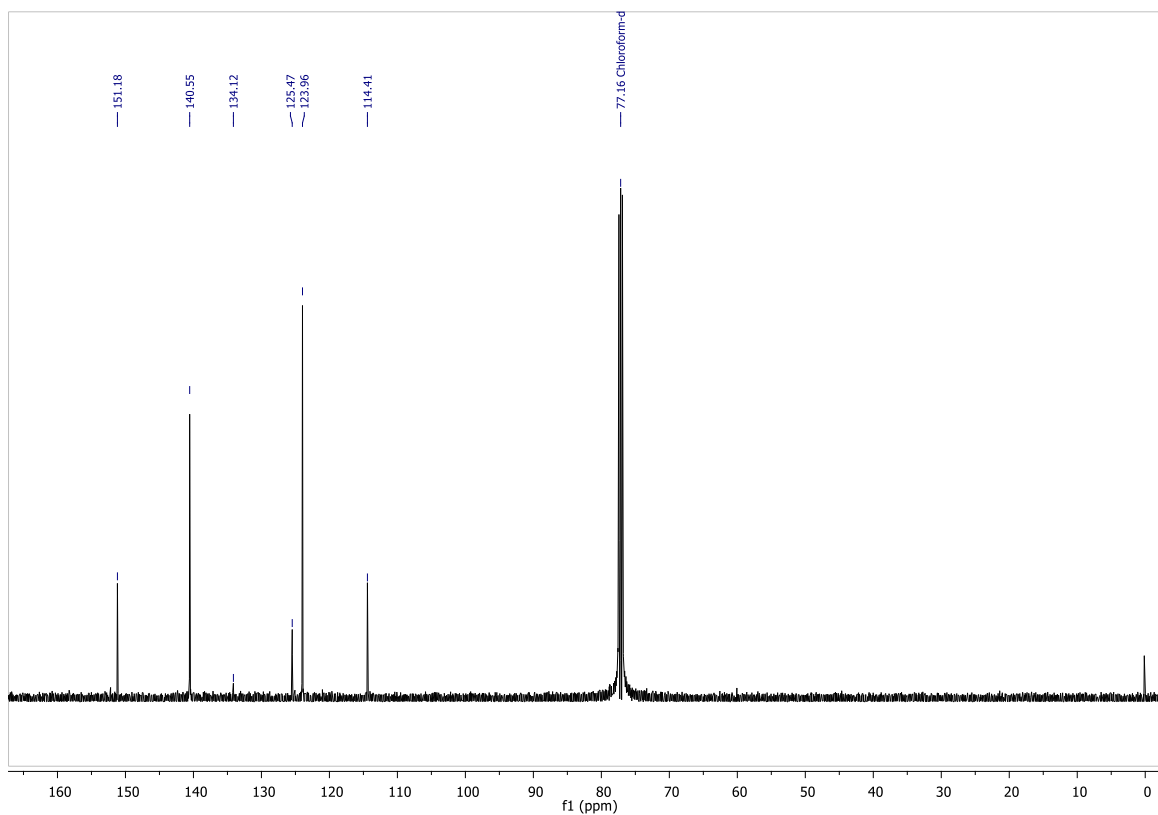
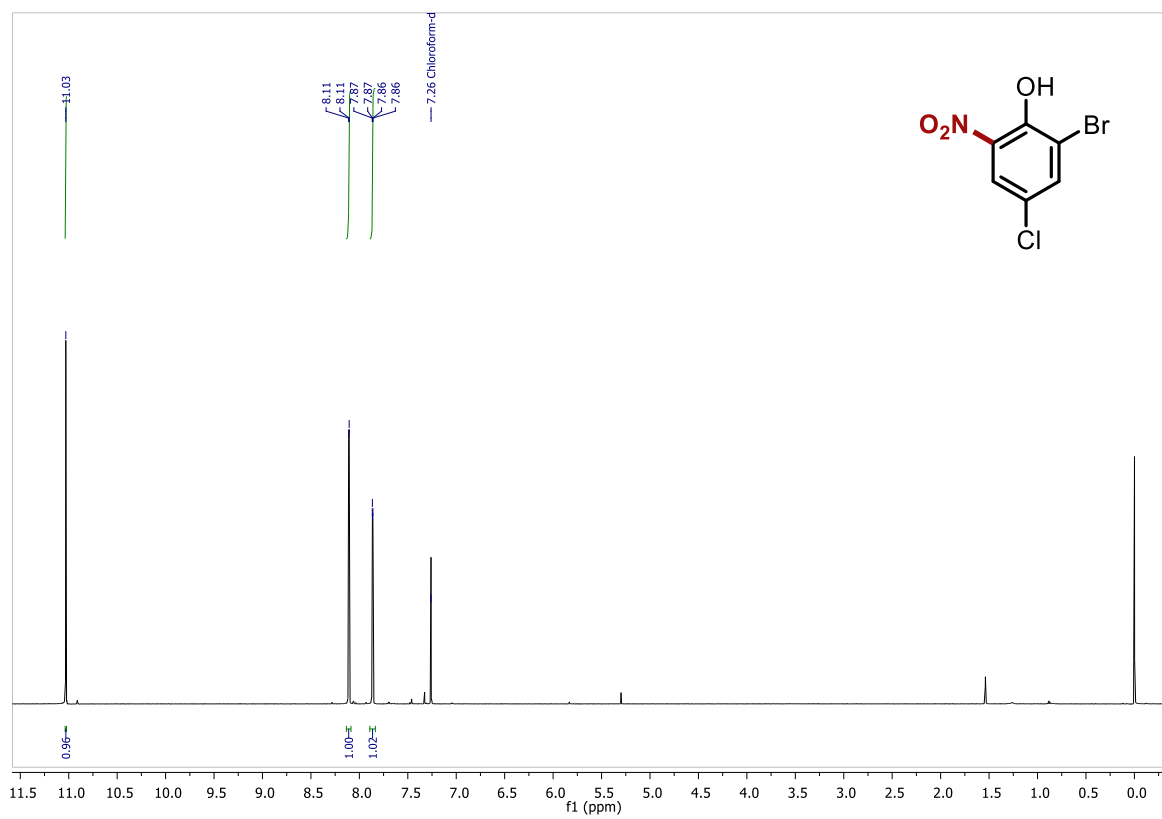
4-hydroxy-3-nitrobenzonitrile (14)



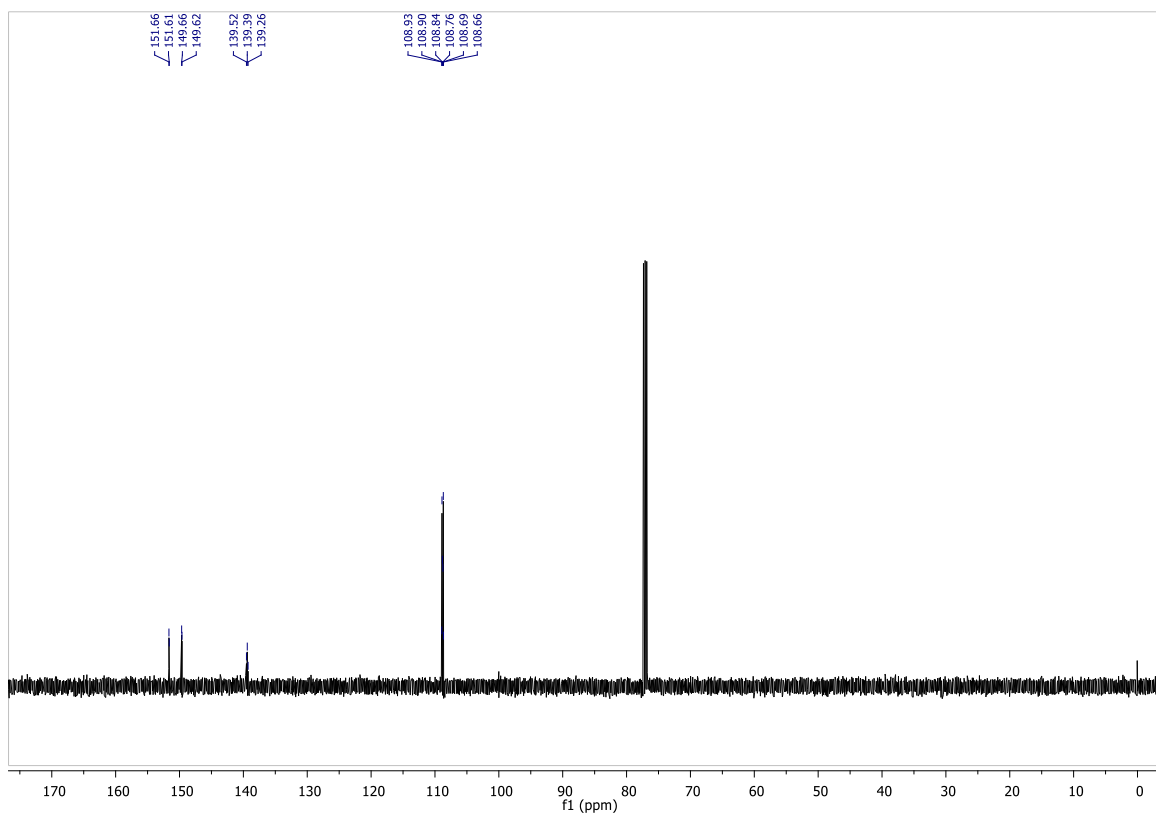
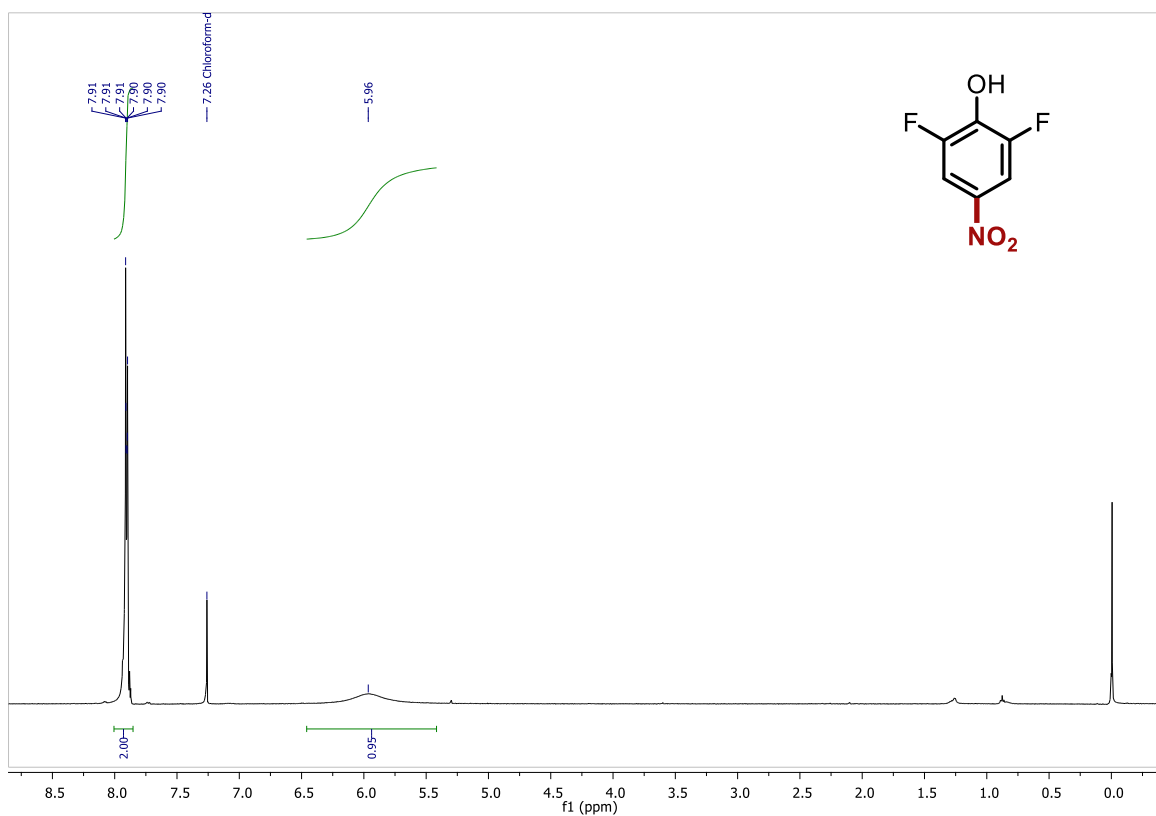
2,4-dinitrophenol (15)



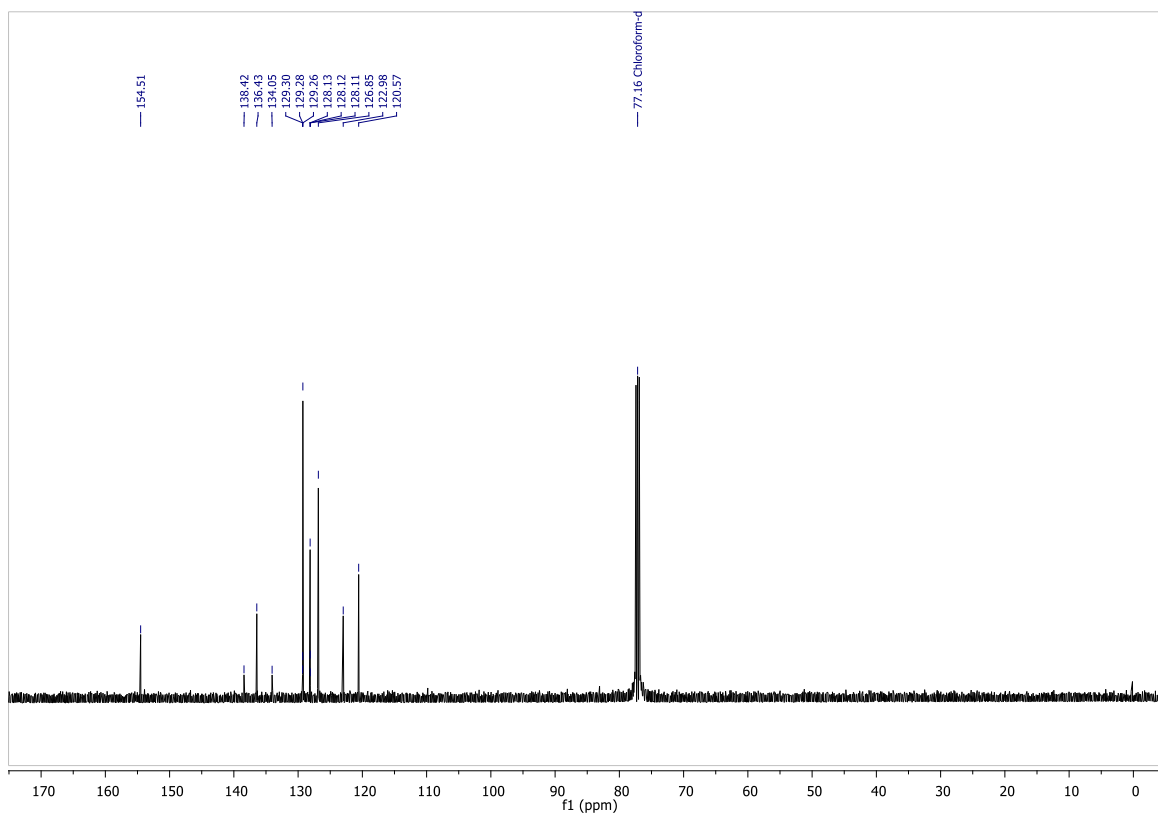
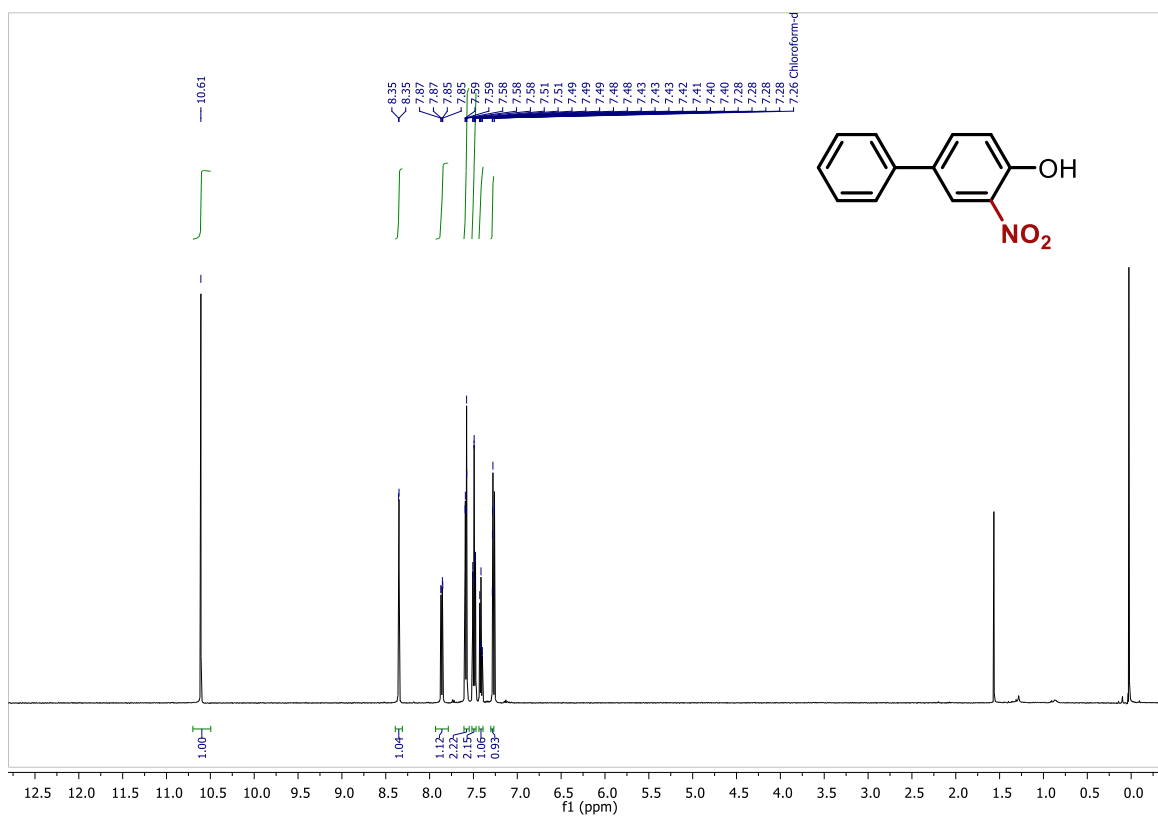
2-bromo-4-chloro-6-nitrophenol (16)



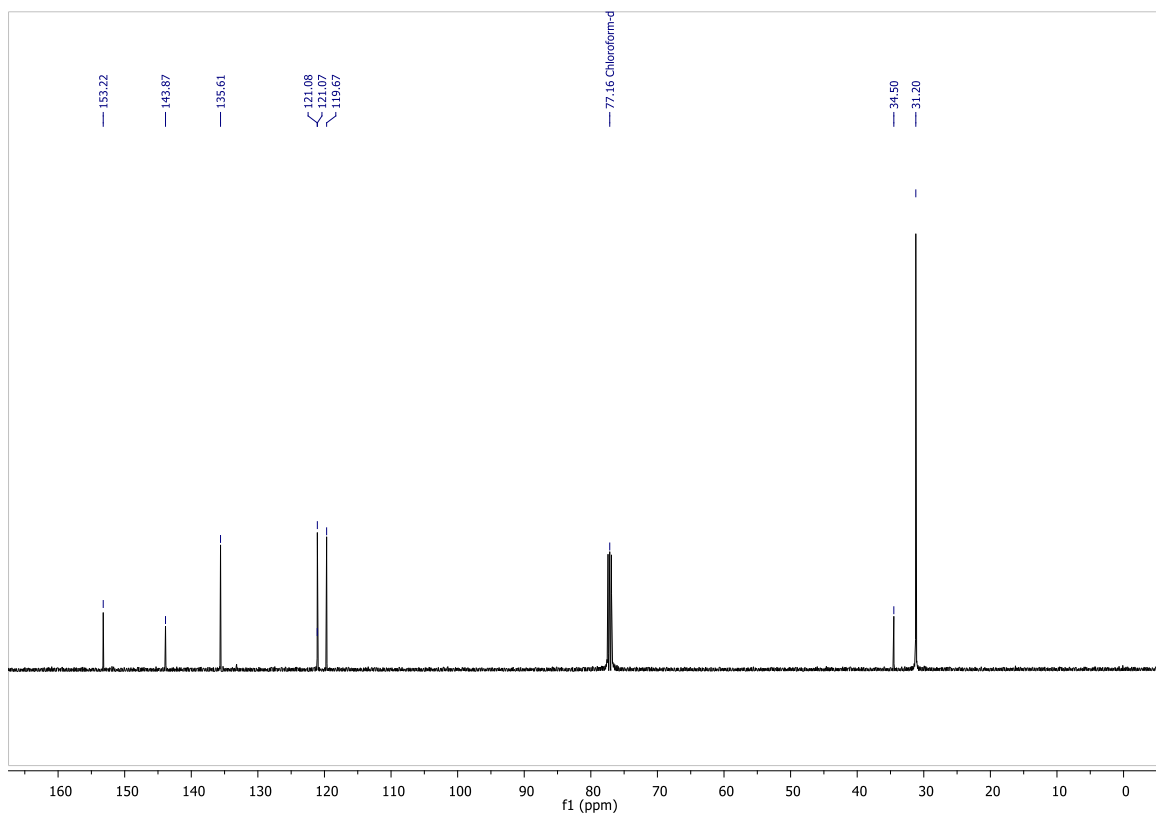
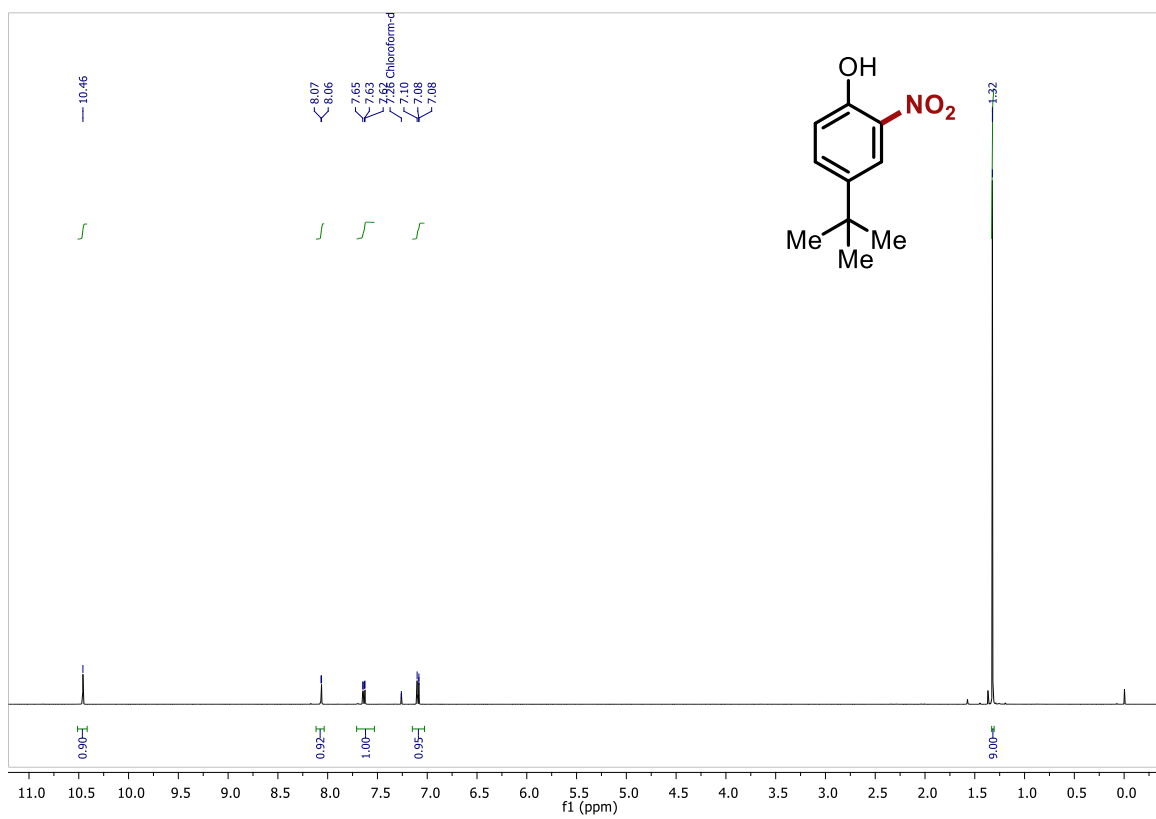
2,6-difluoro-4-nitrophenol (17)



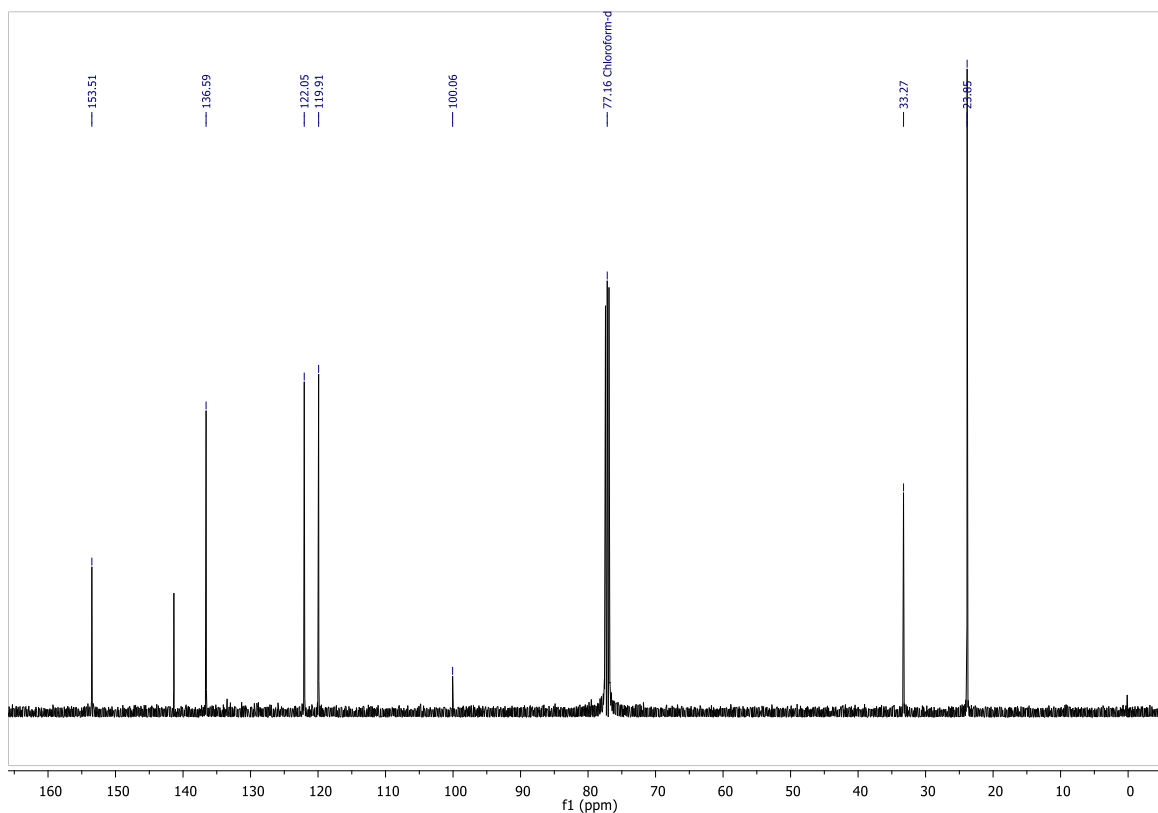
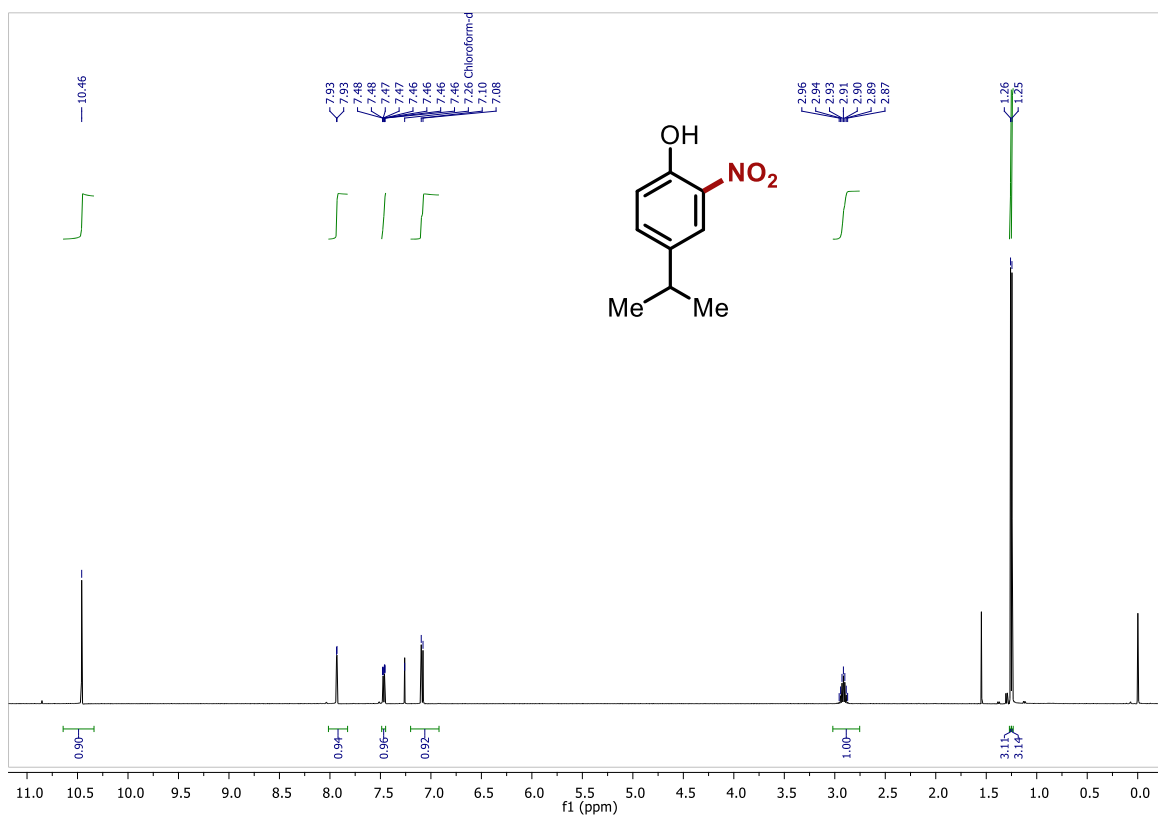
3-nitro-[1,1'-biphenyl]-4-ol (18)



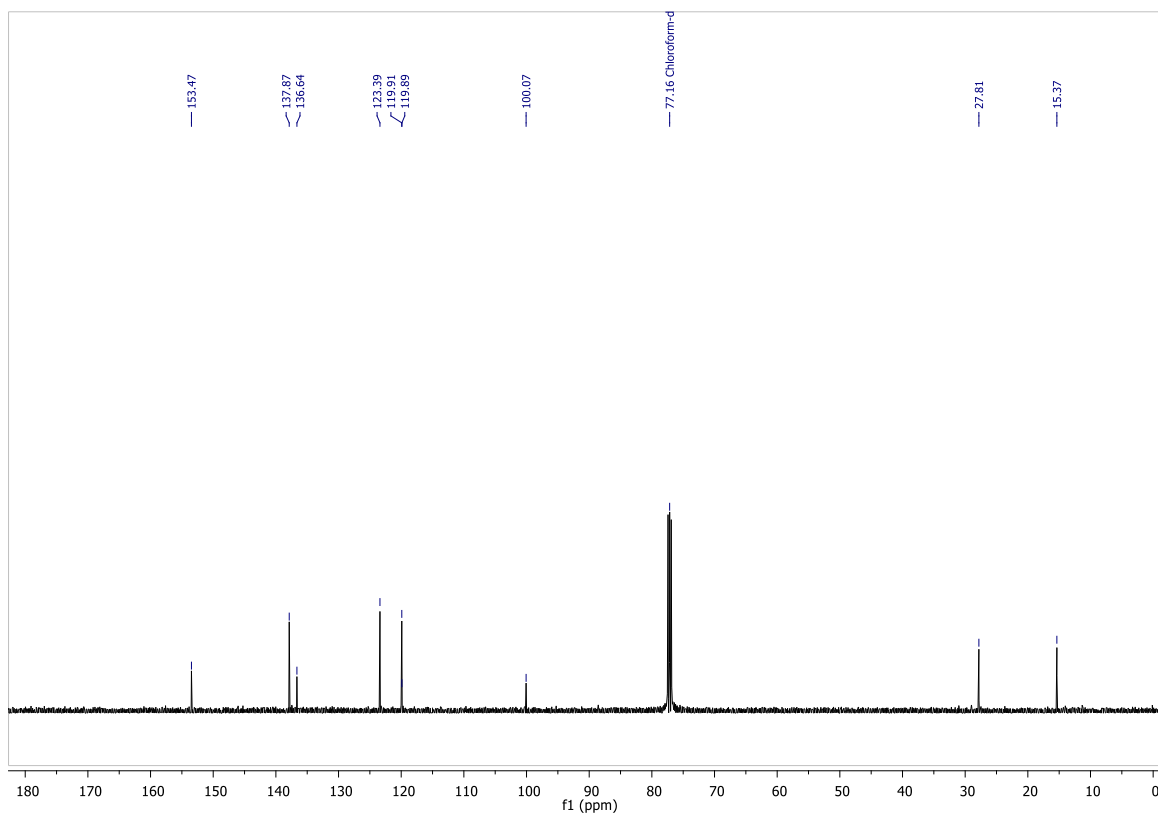
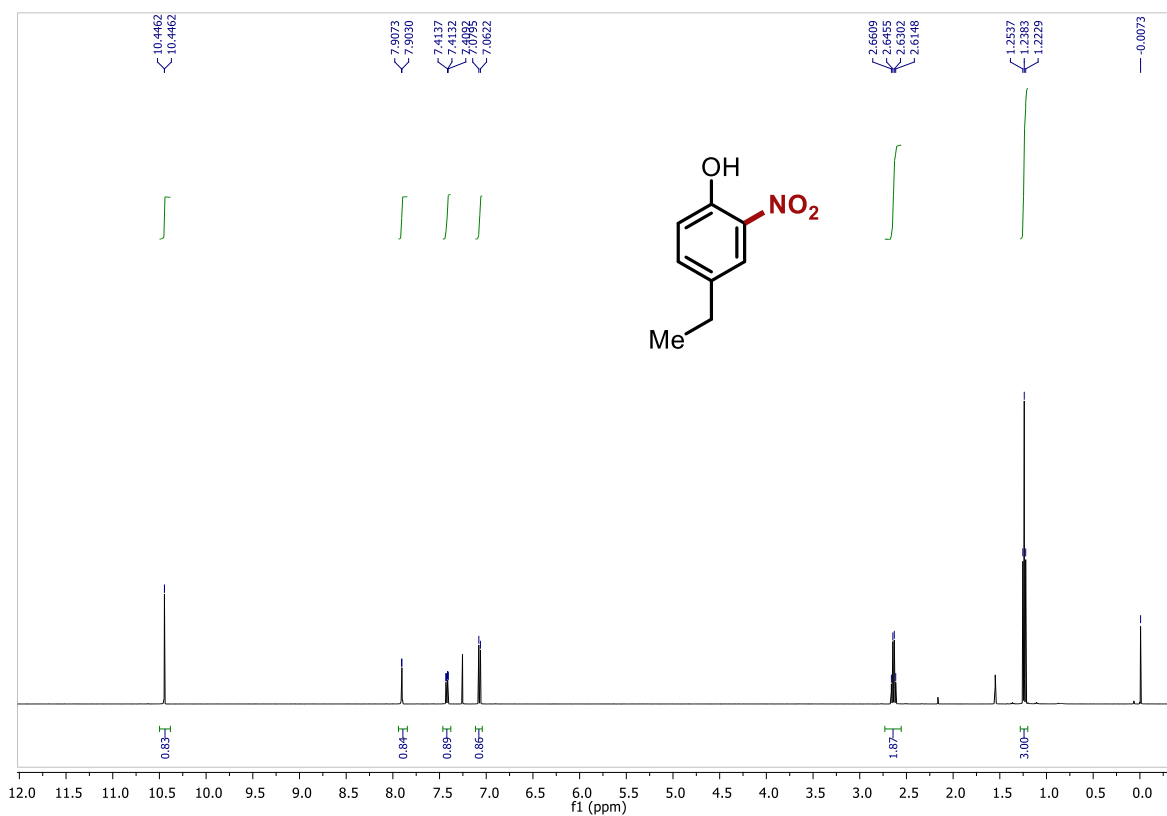
4-(*tert*-butyl)-2-nitrophenol (19)



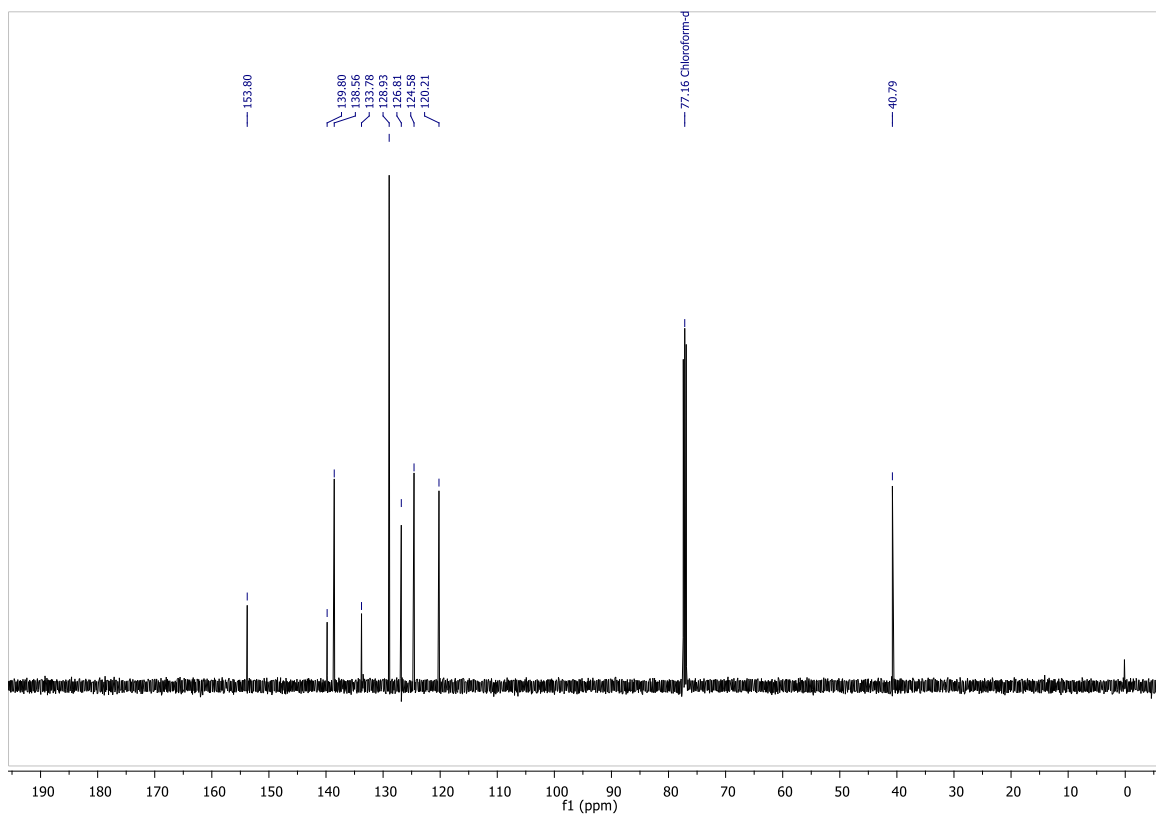
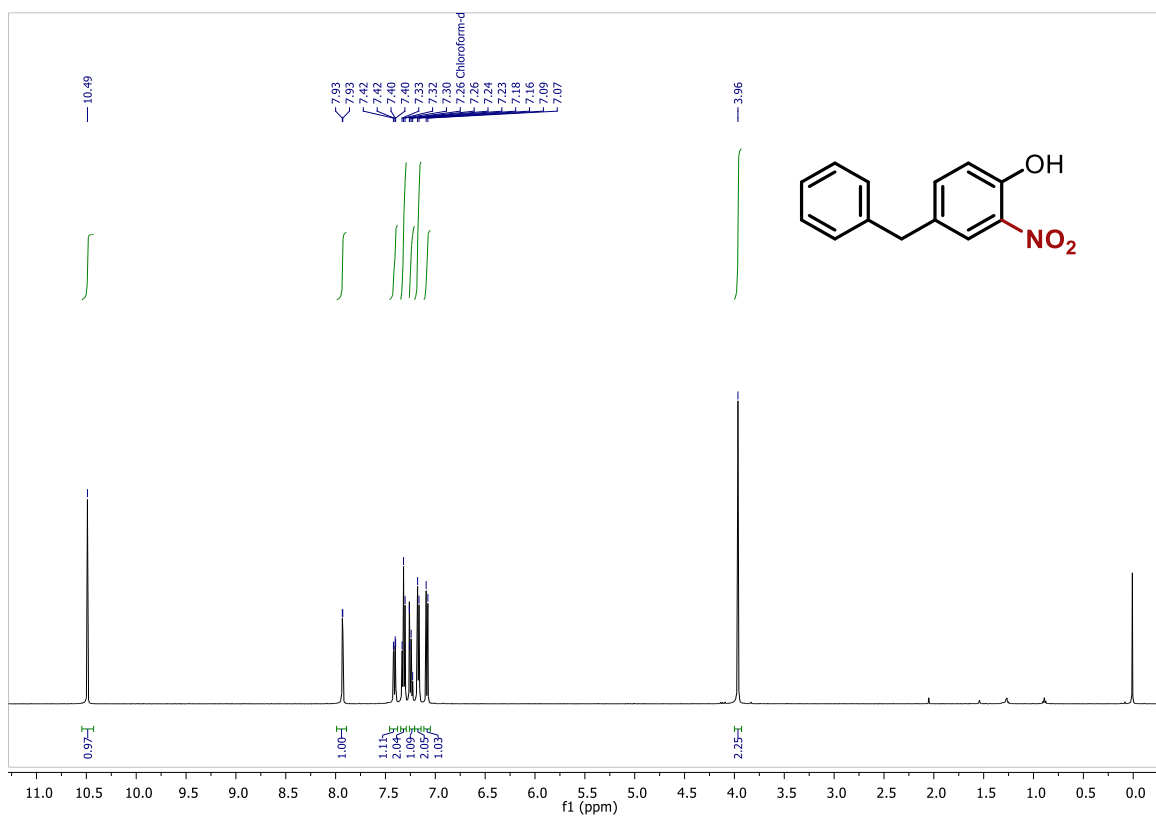
4-isopropyl-2-nitrophenol (20)



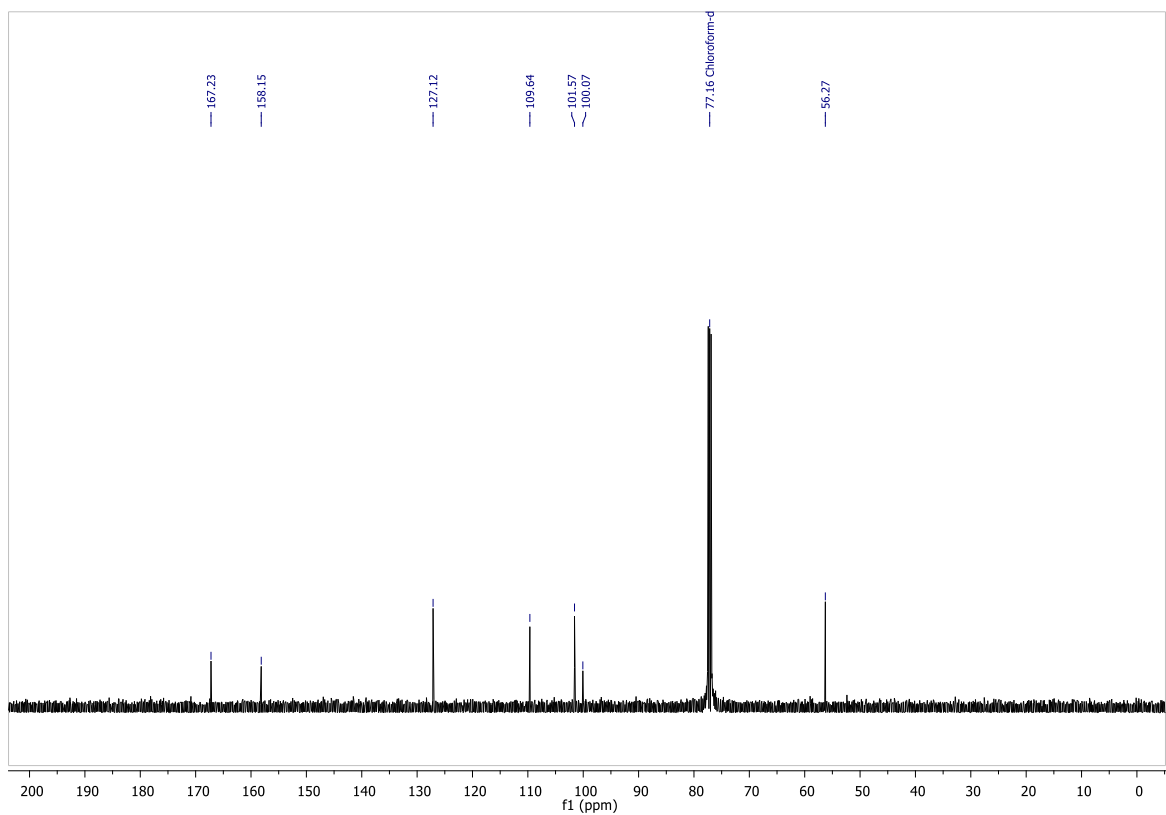
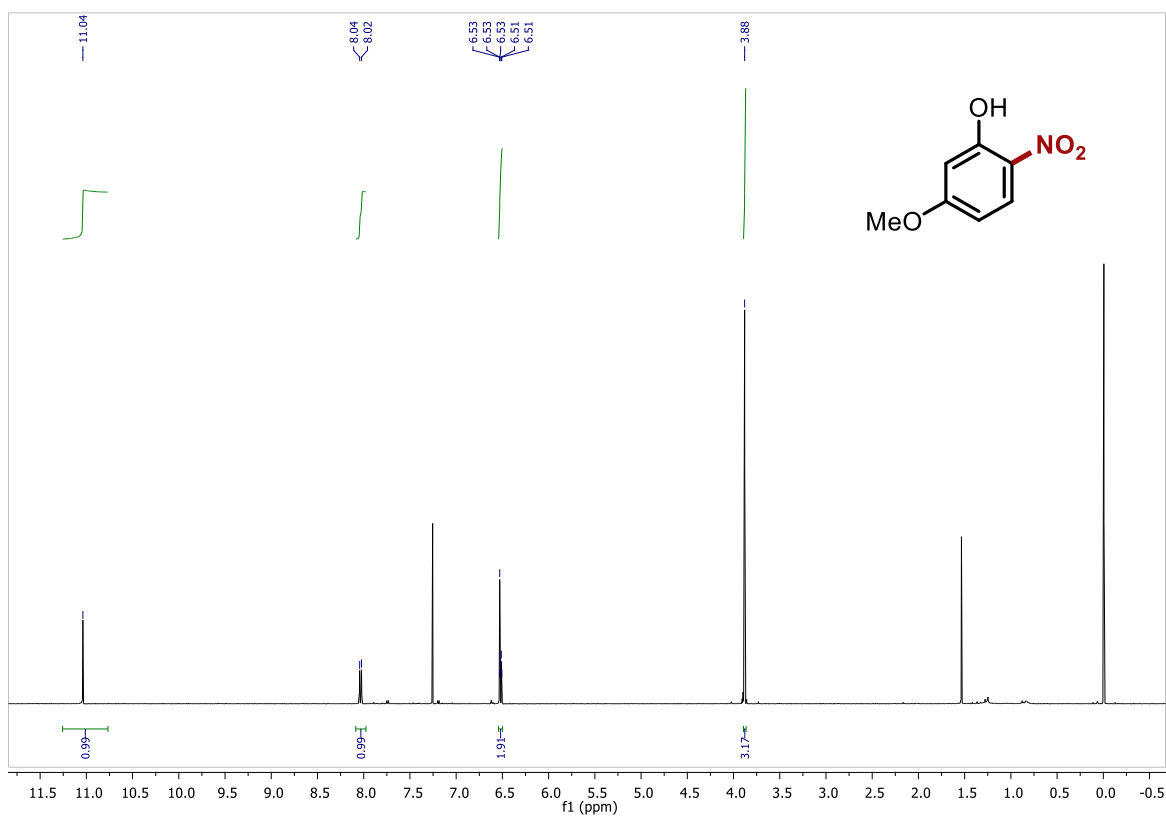
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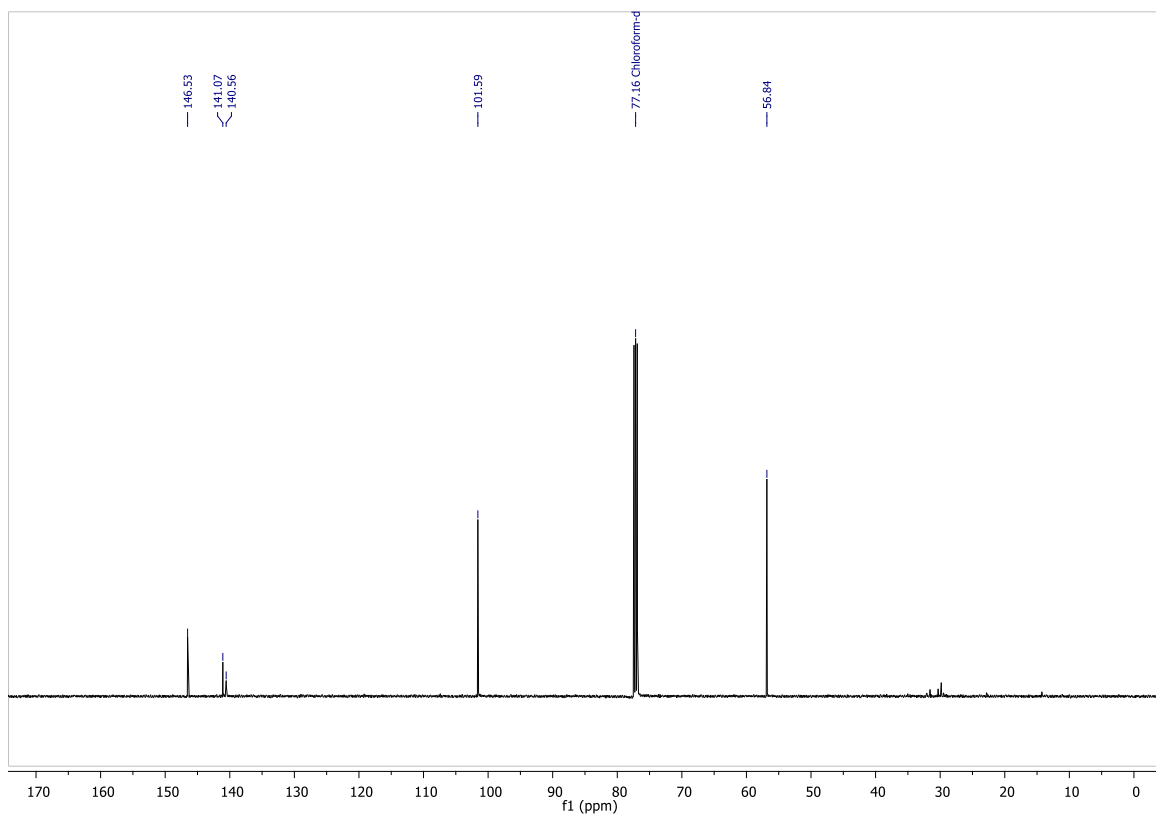
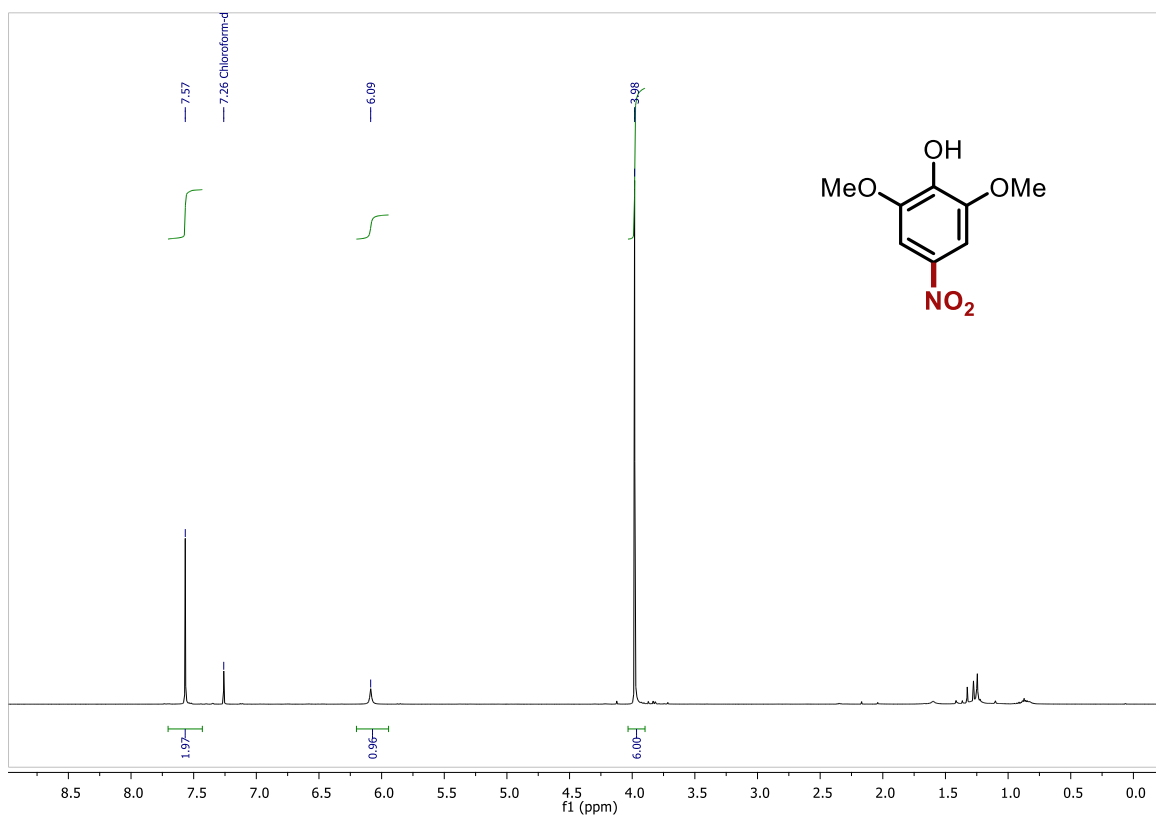
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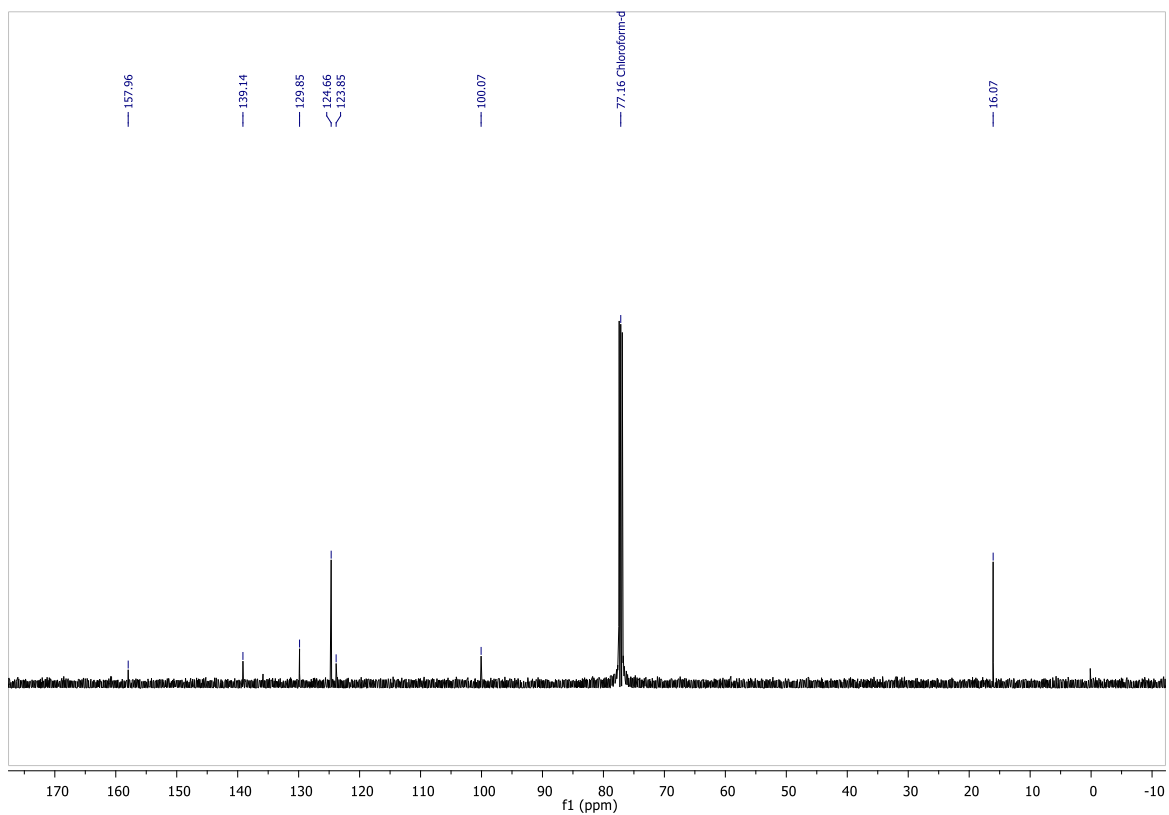
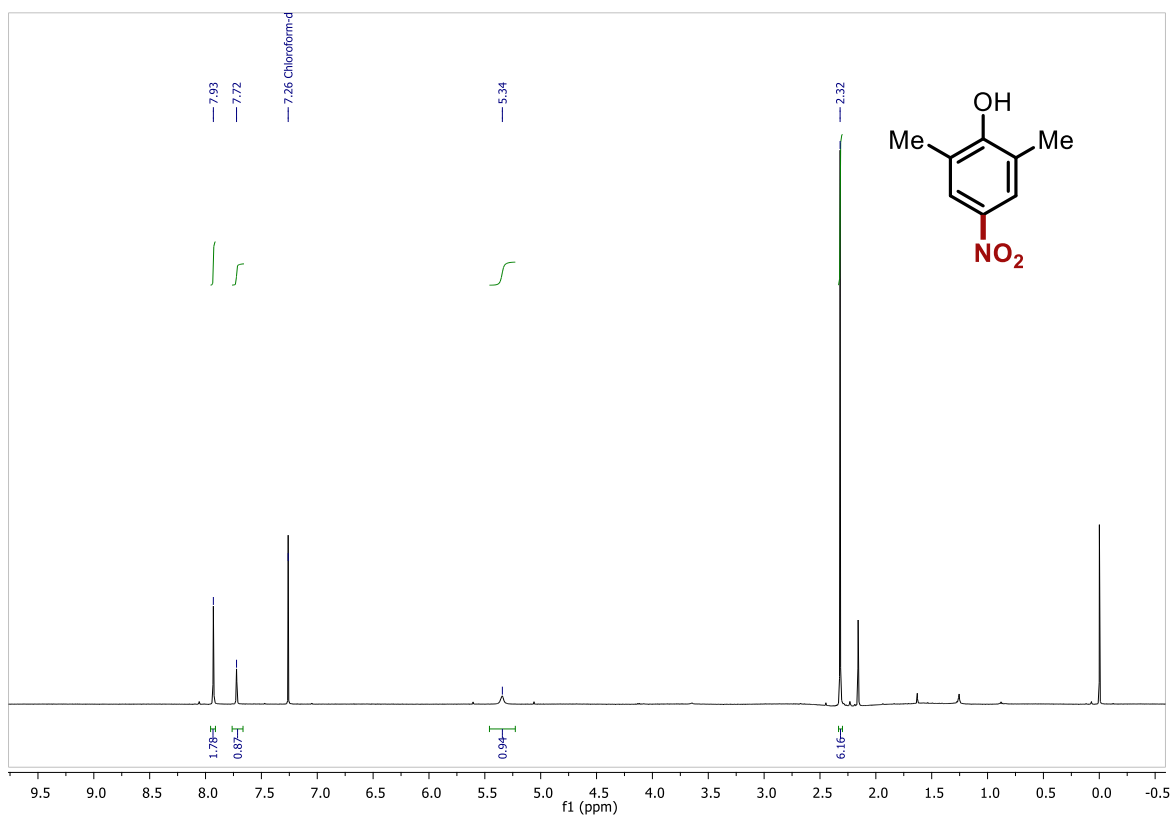
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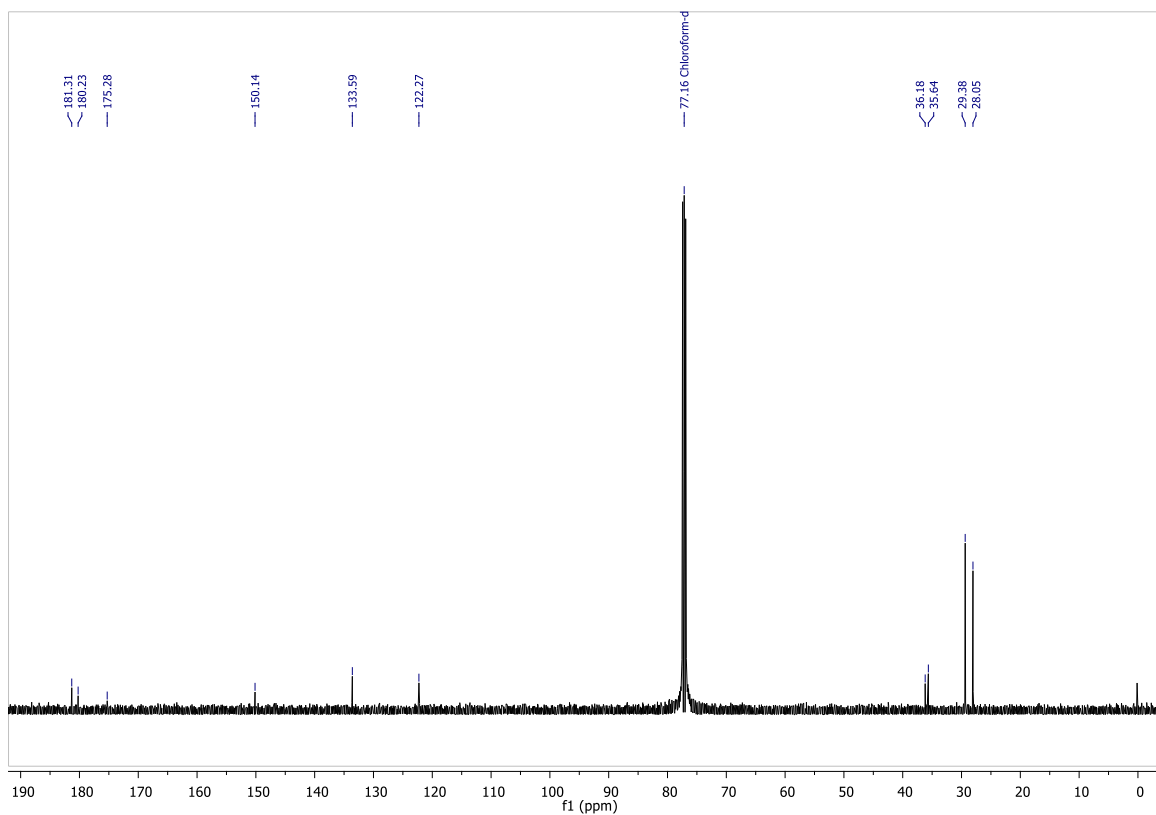
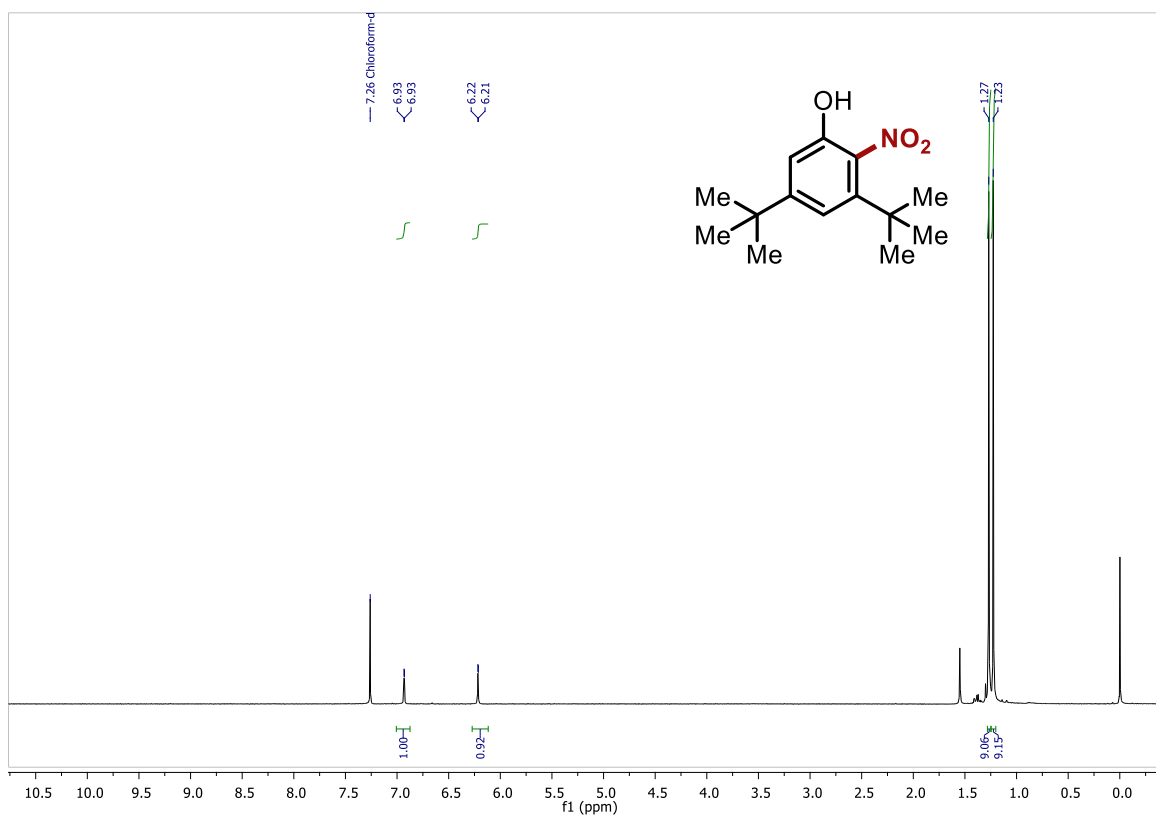
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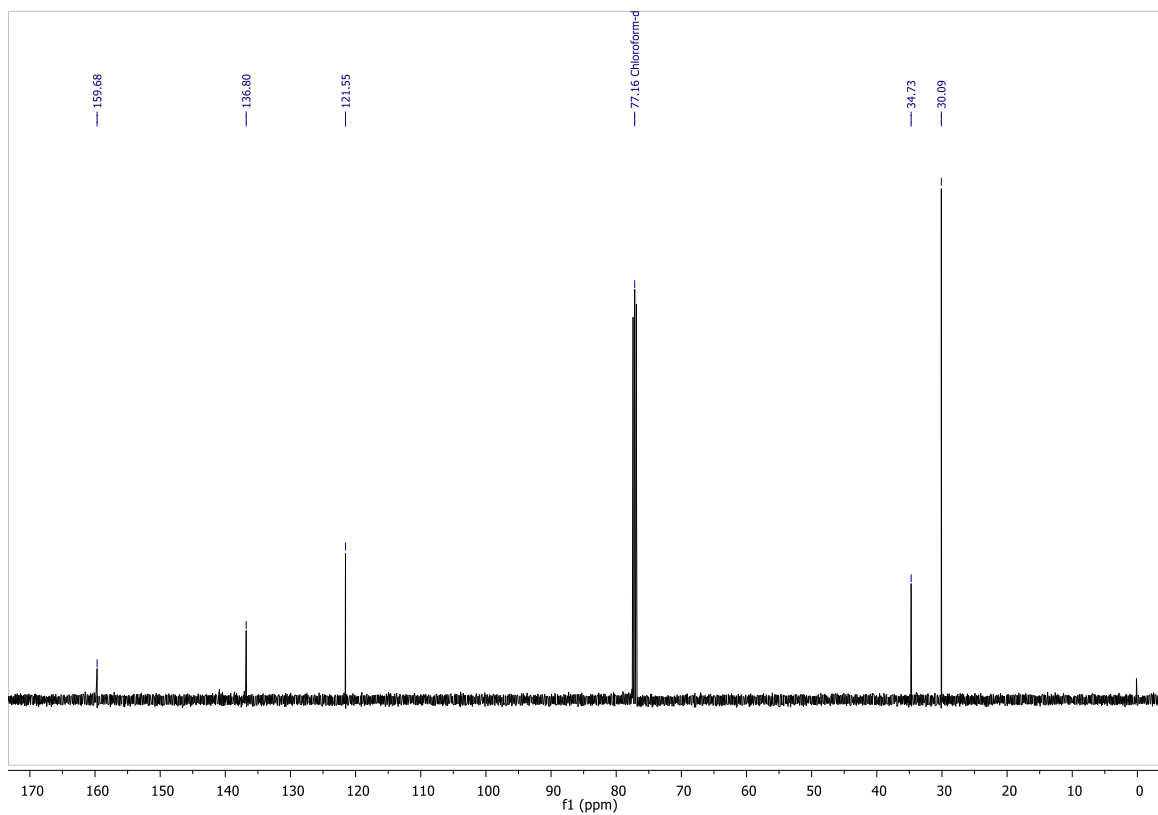
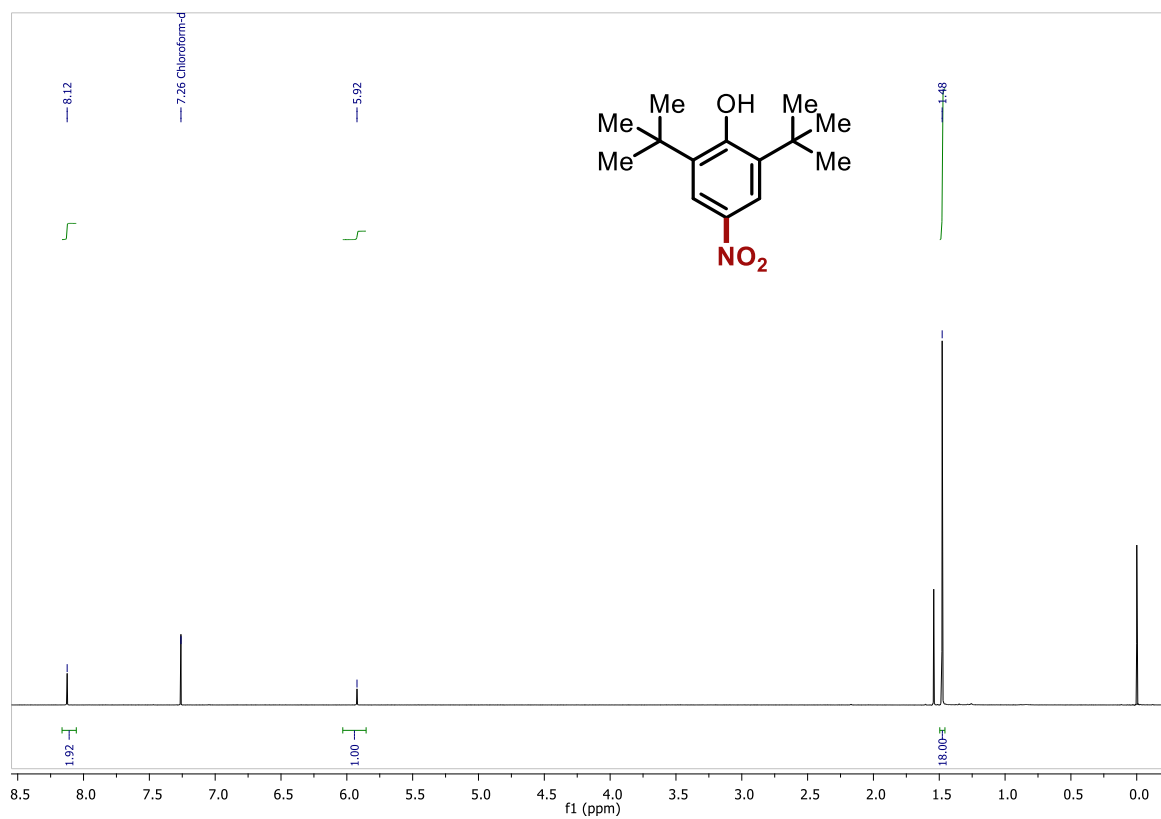
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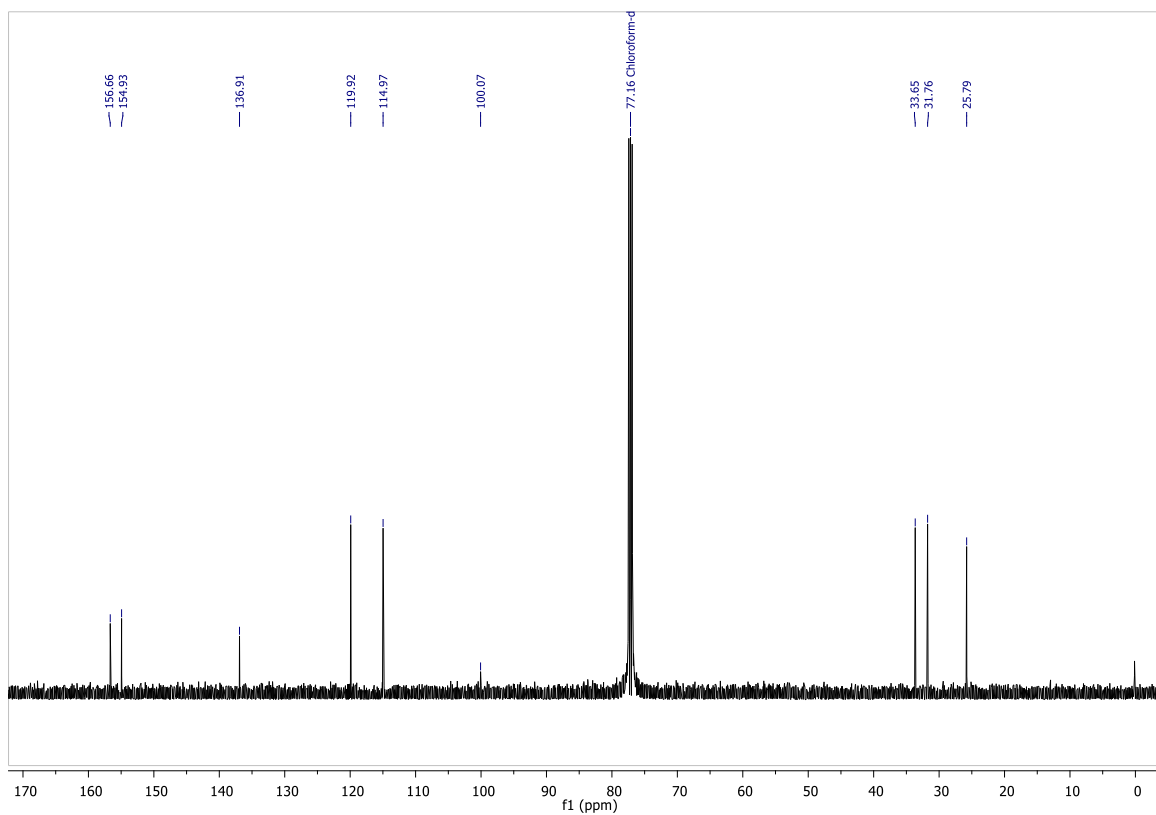
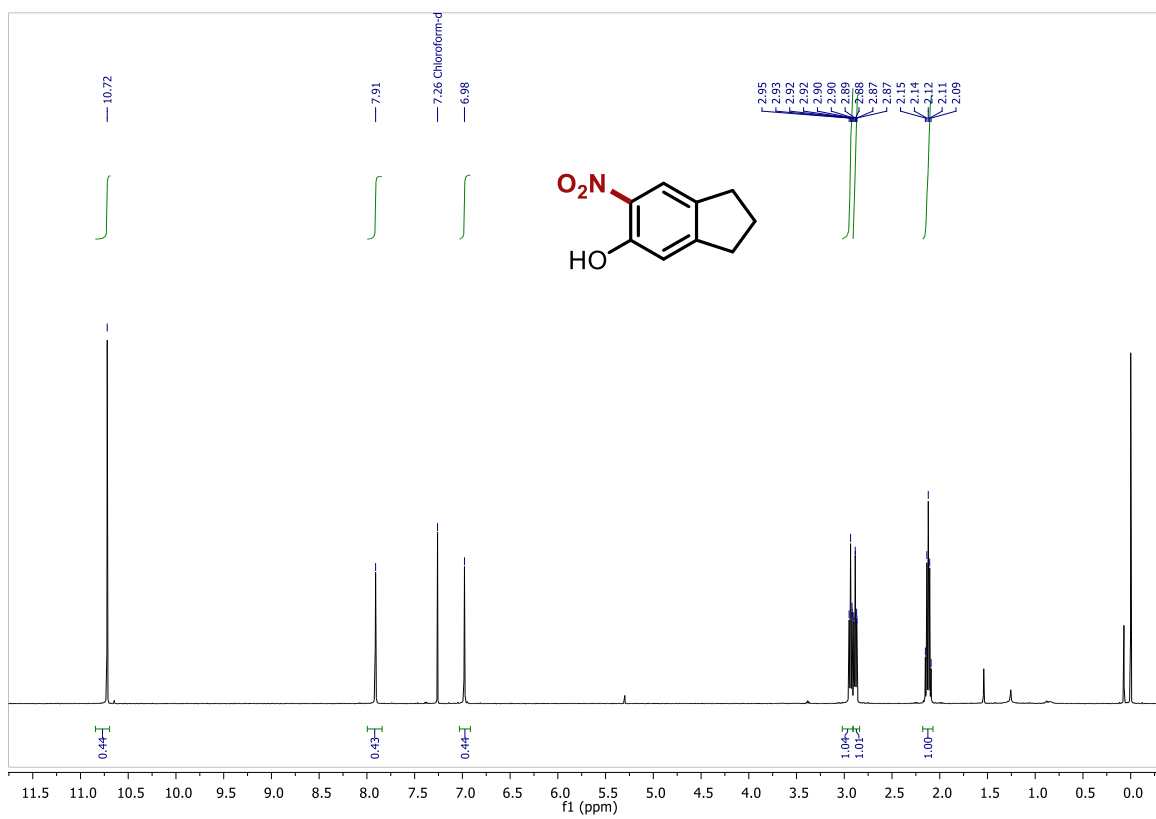
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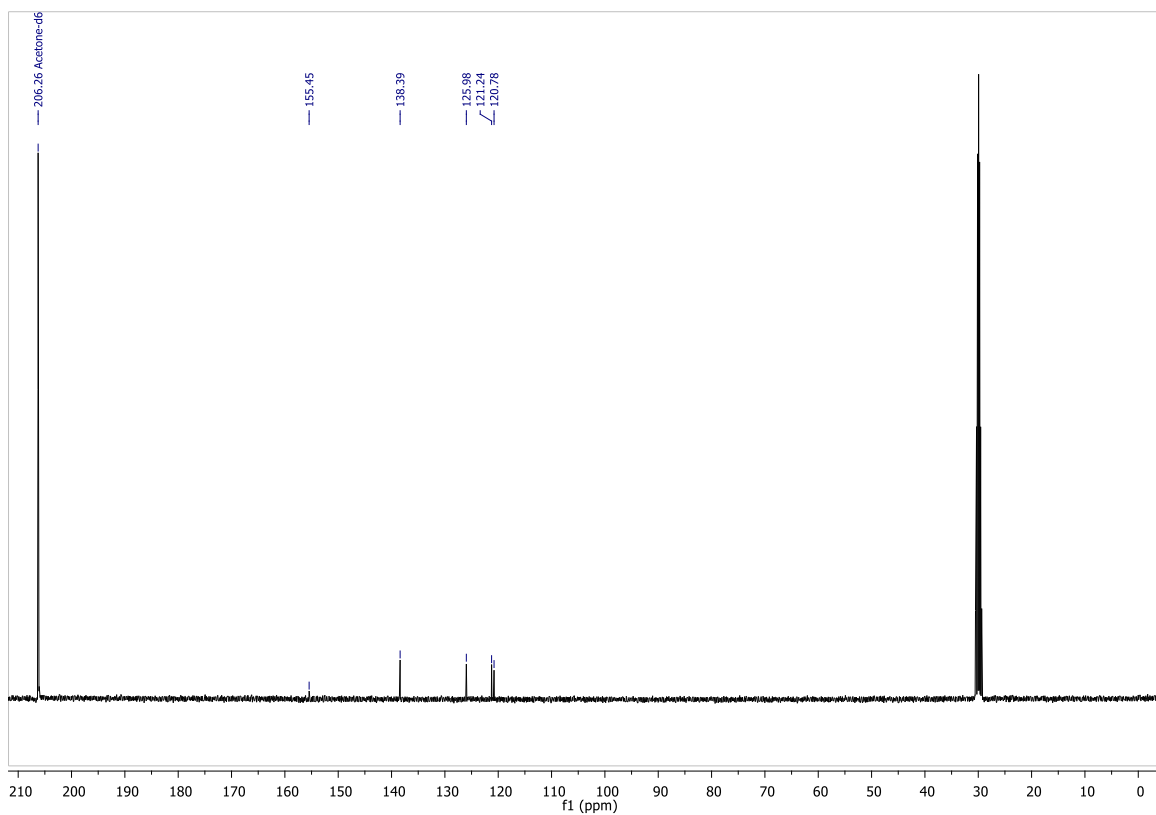
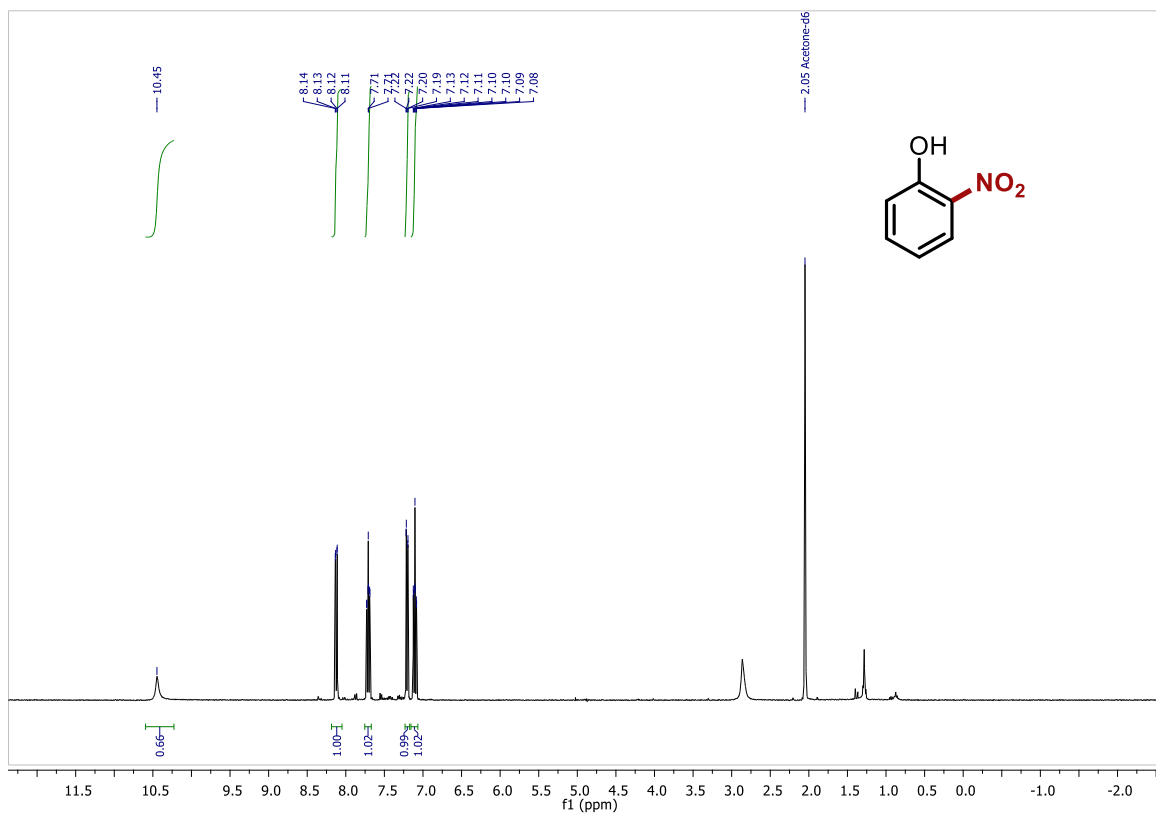
2,6-di-*tert*-butyl-4-nitrophenol (27)



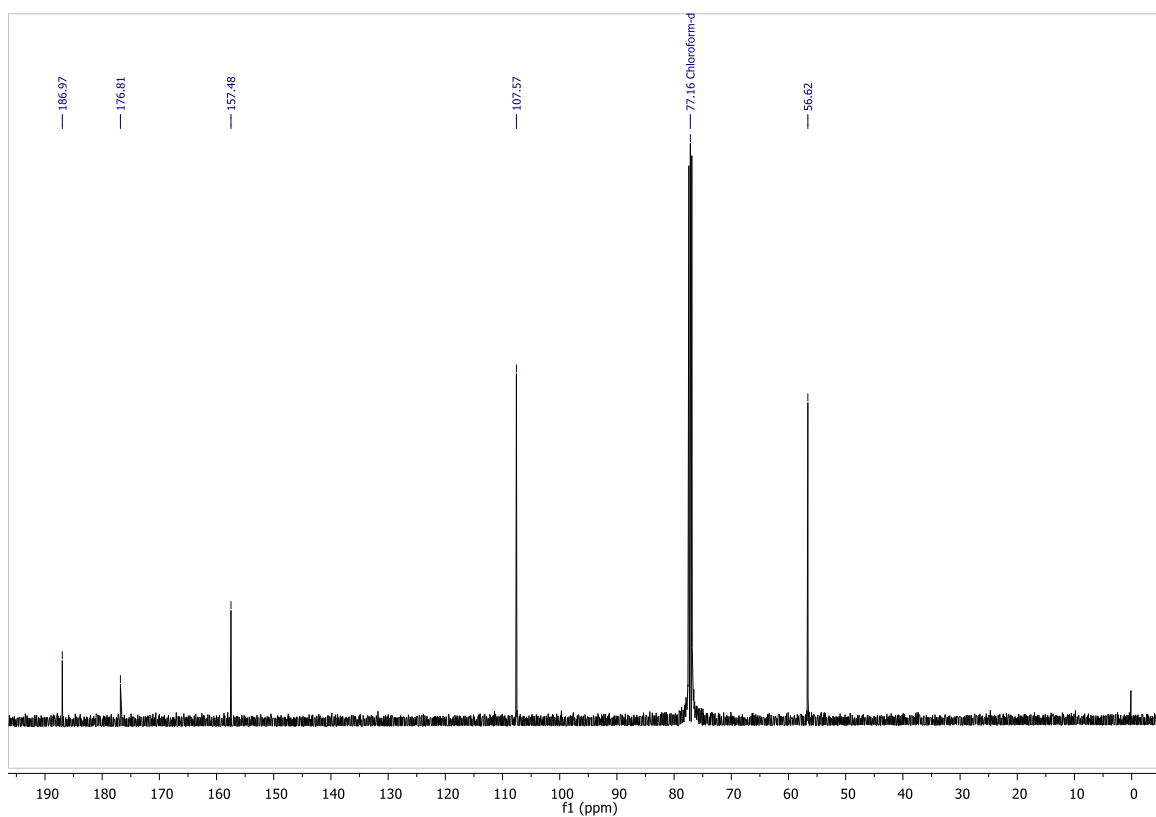
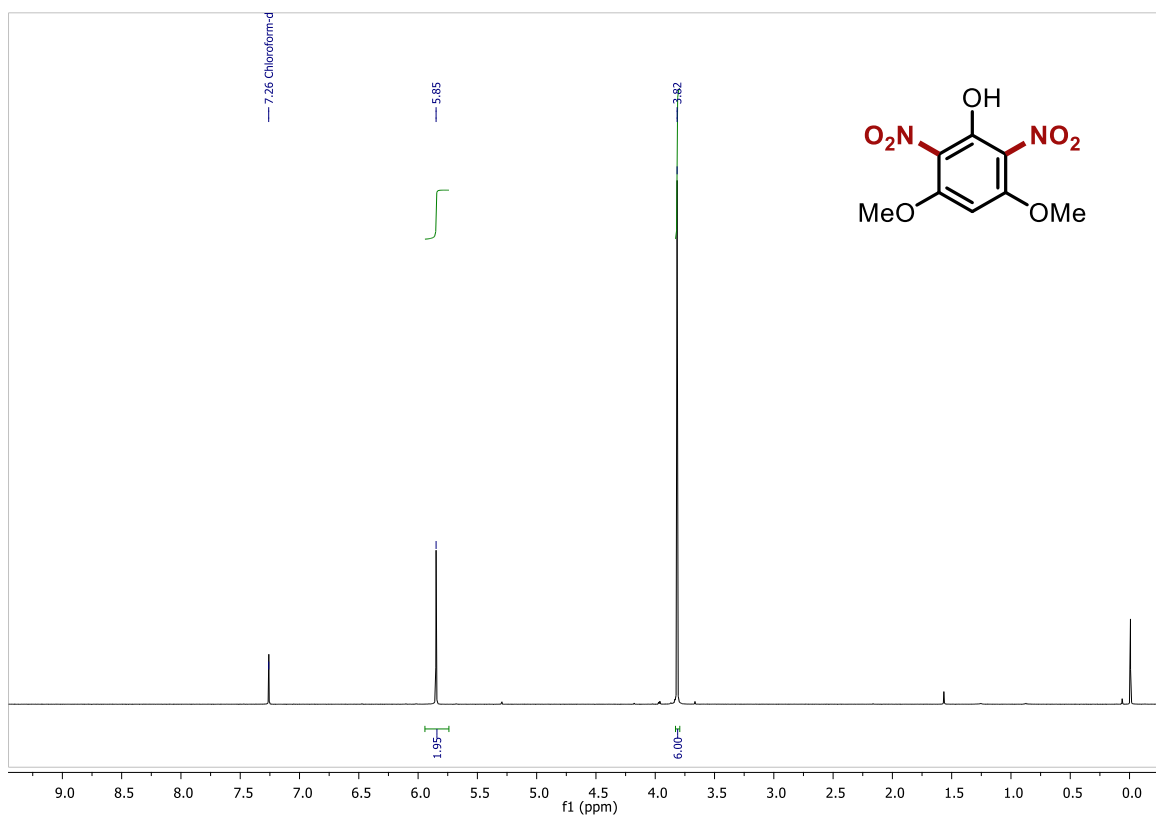
6-nitro-2,3-dihydro-1H-inden-5-ol (28)



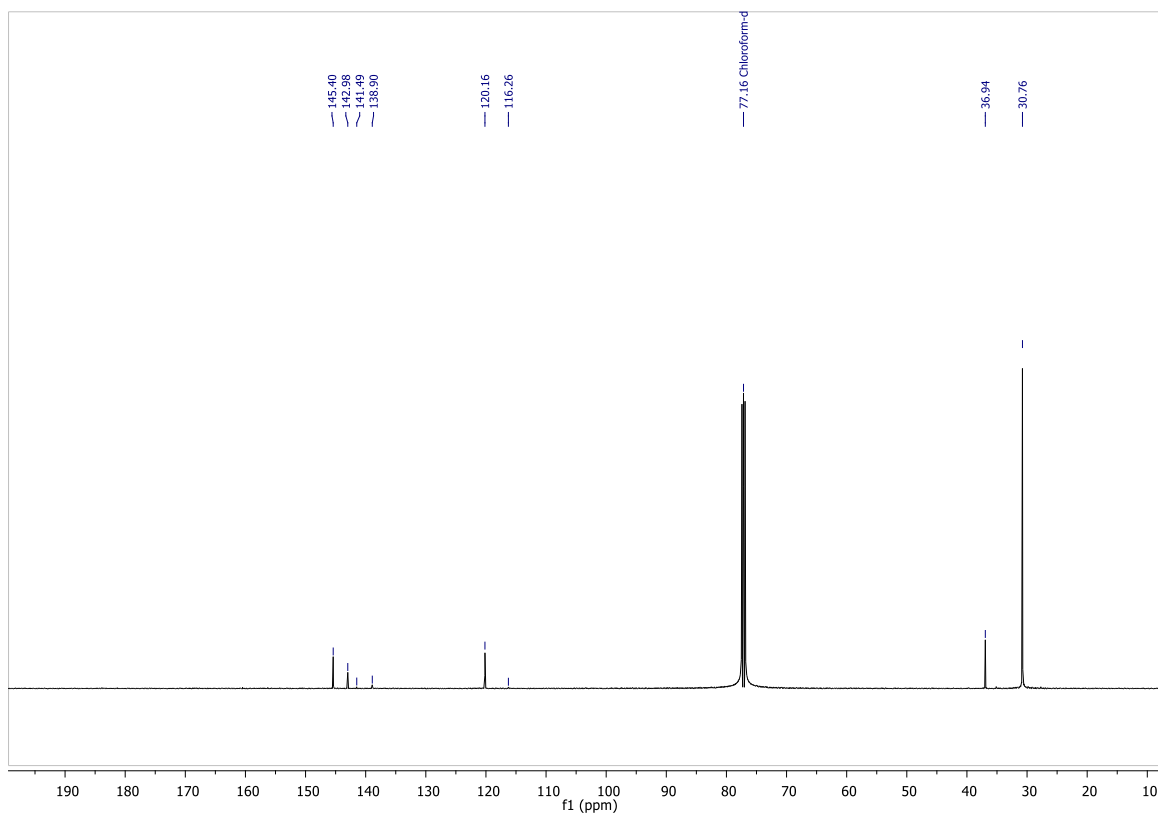
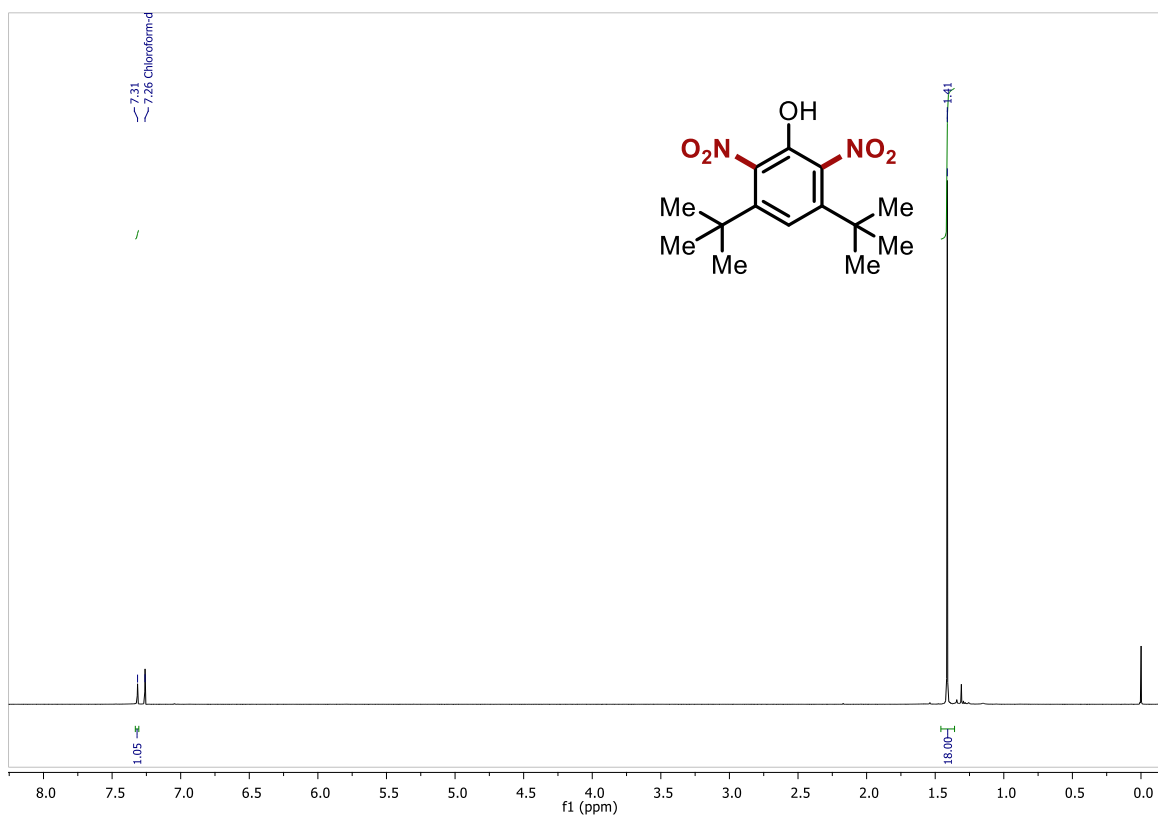
2-nitrophenol (29)



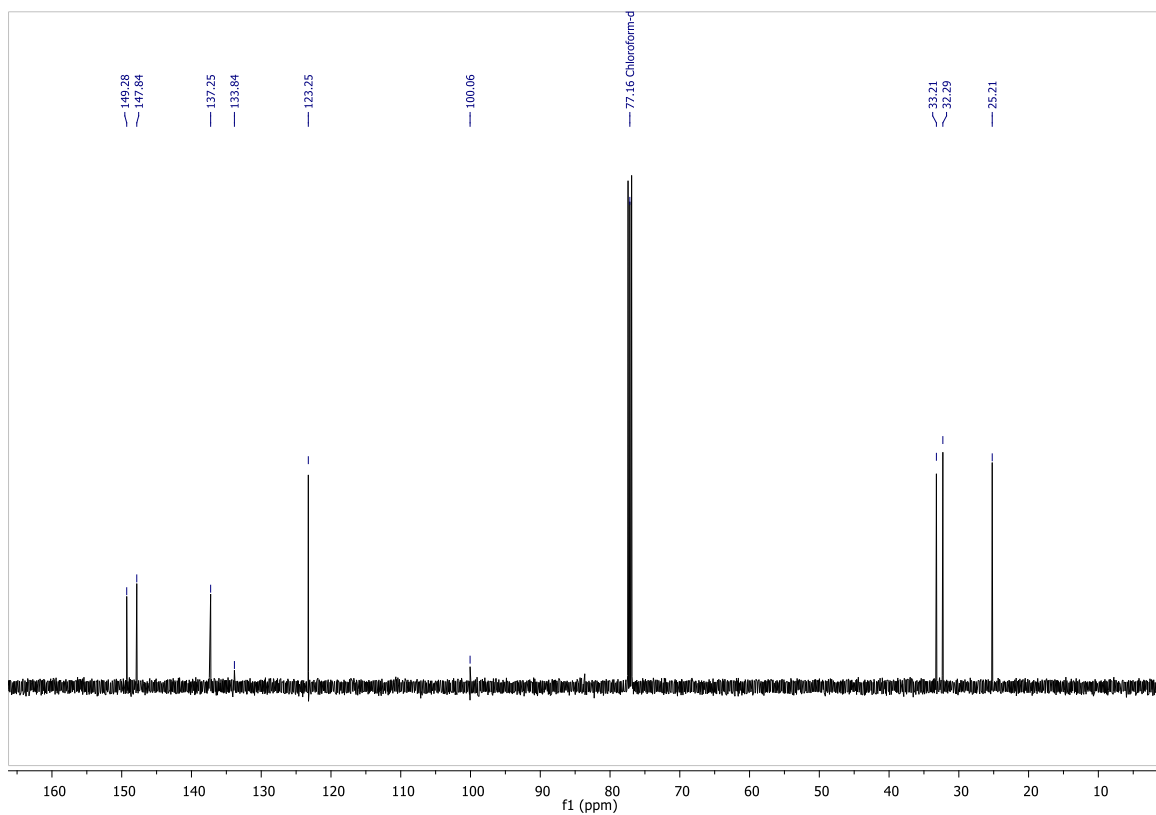
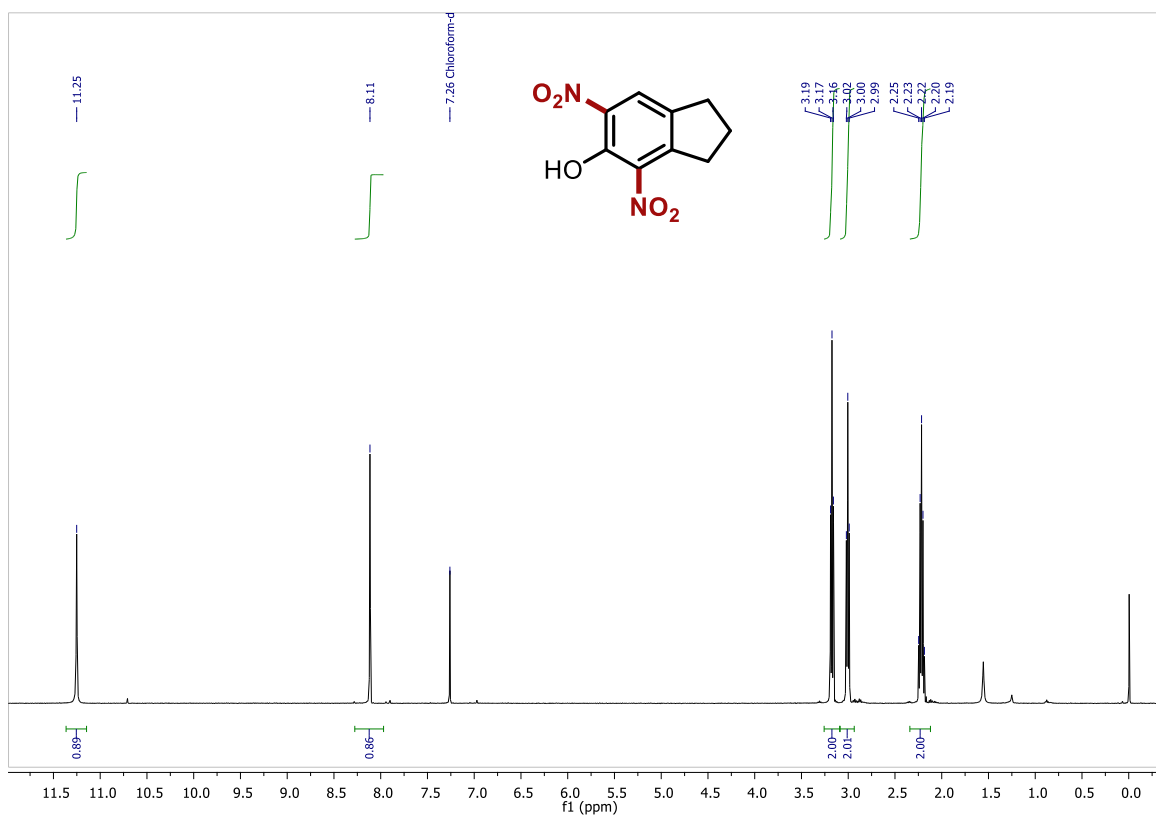
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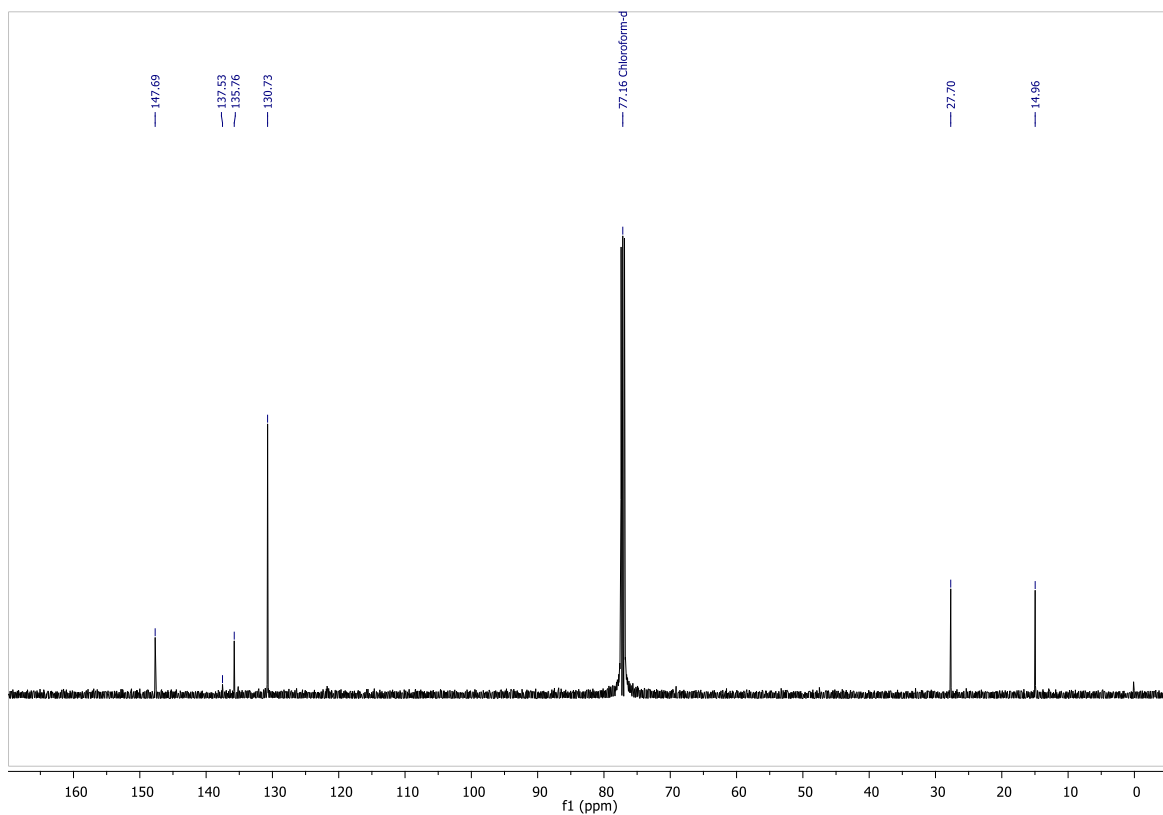
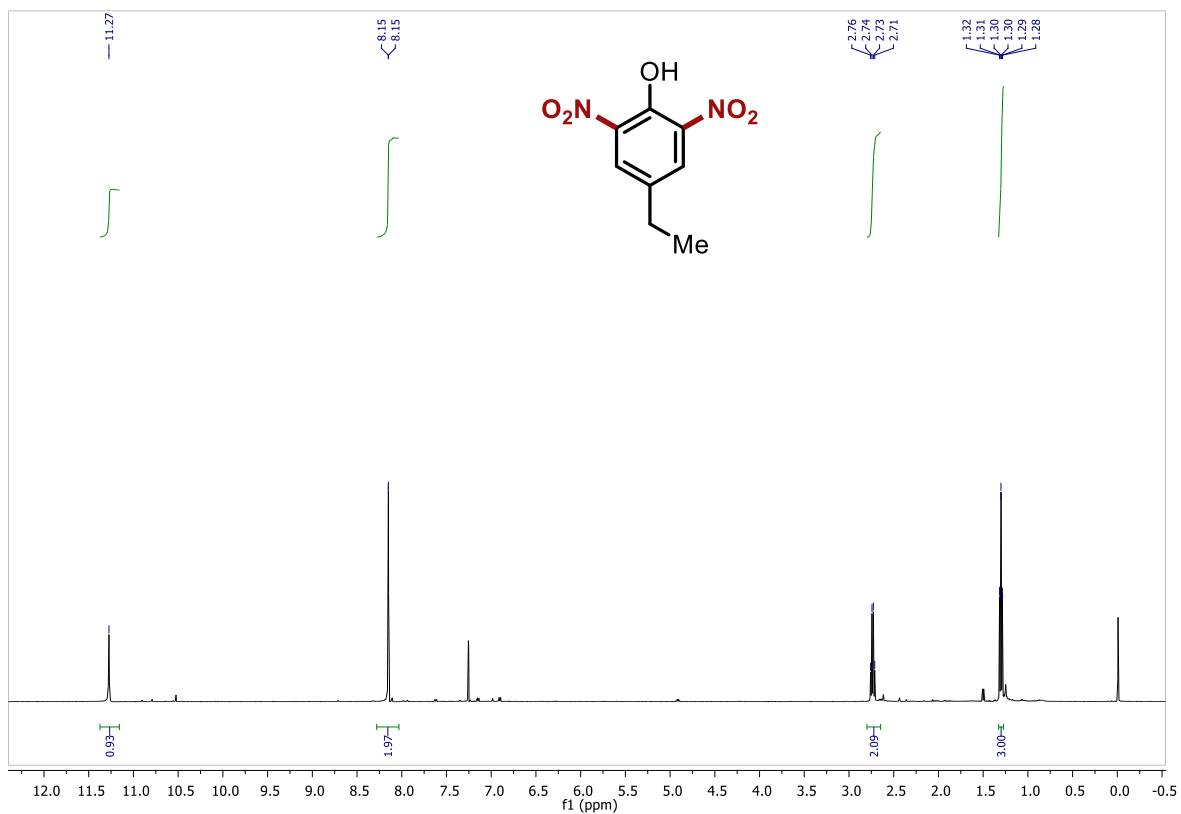
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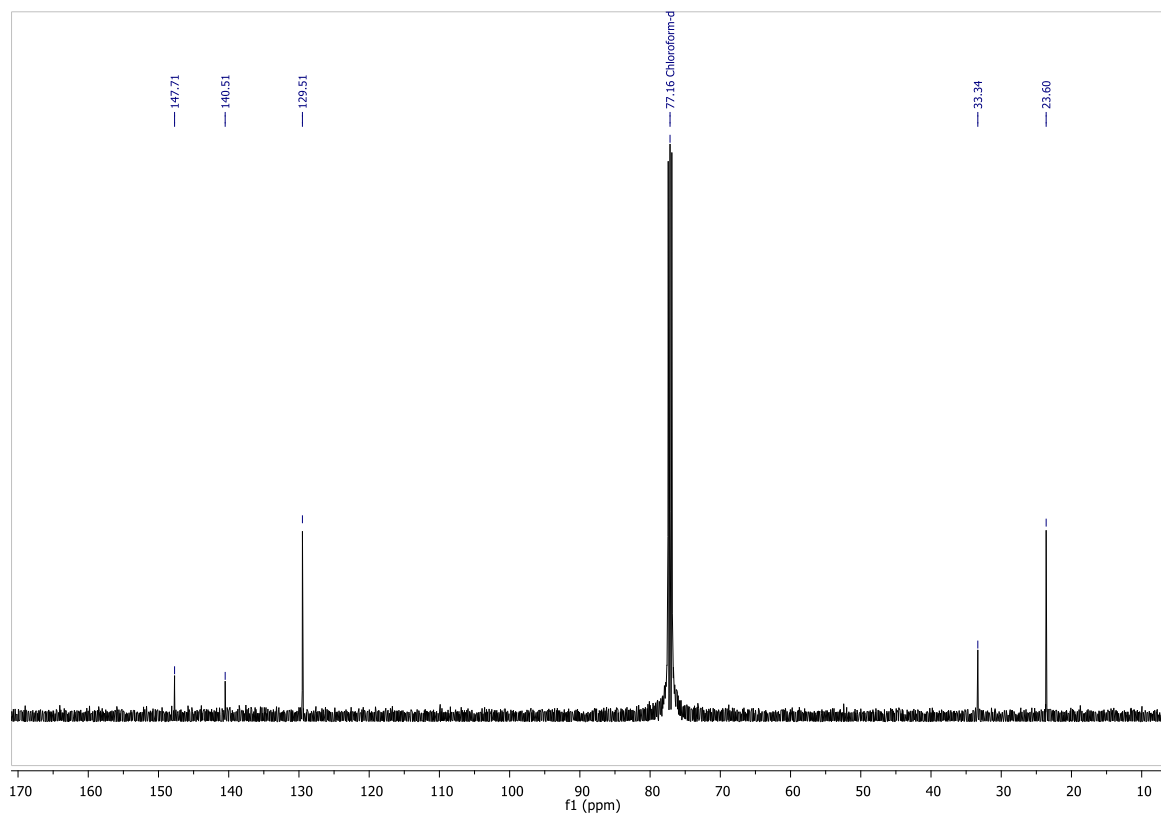
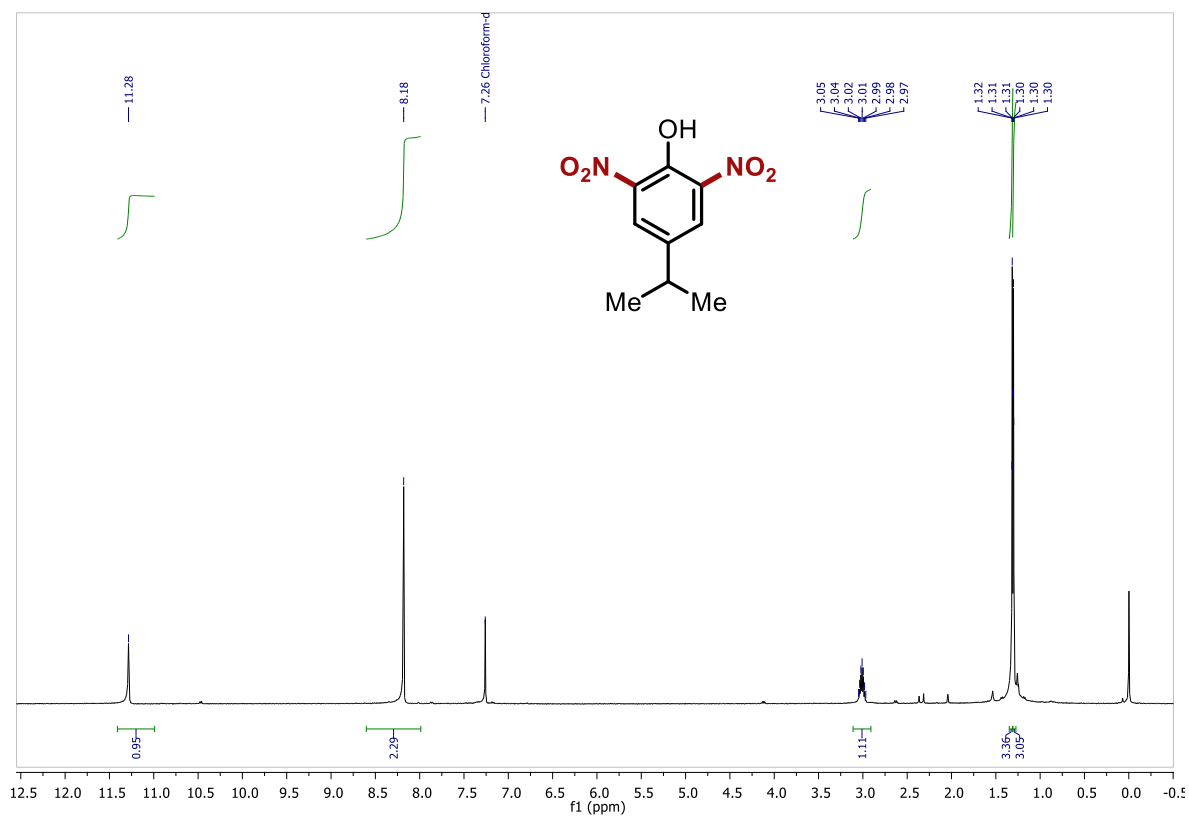
4,6-dinitro-2,3-dihydro-1H-inden-5-ol (32)



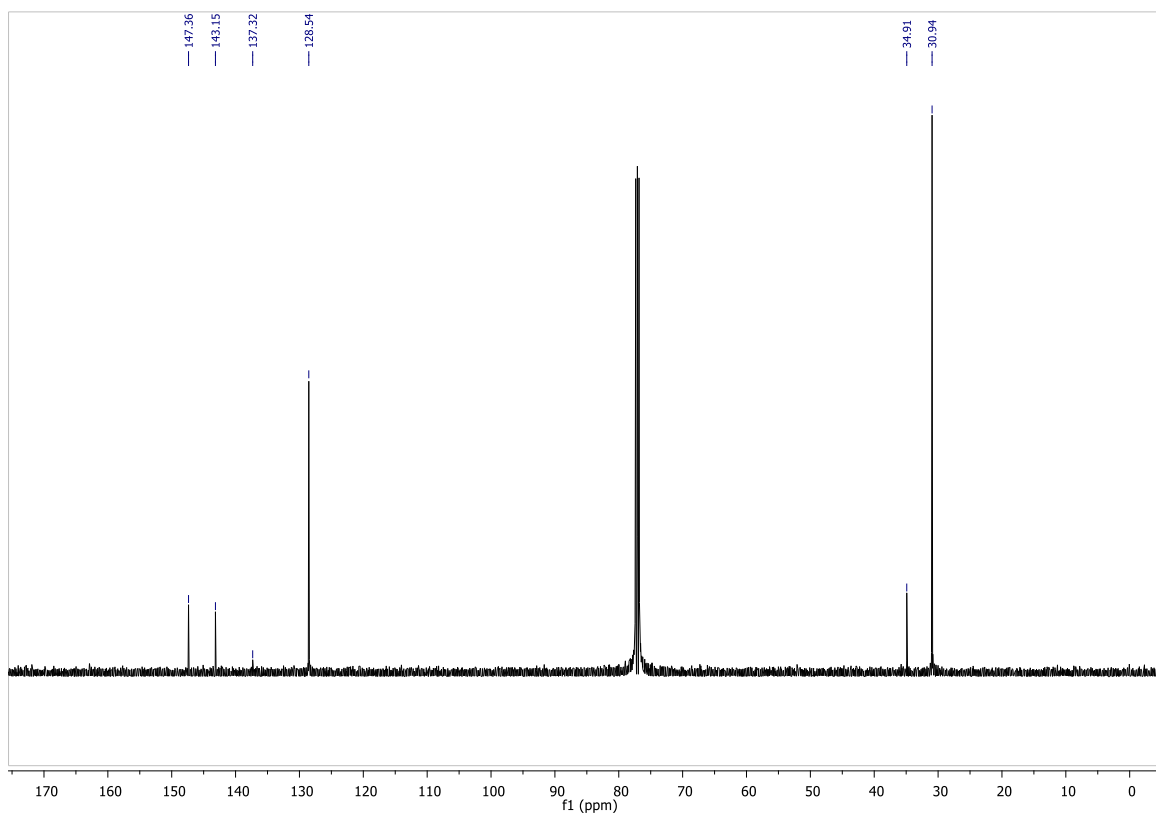
4-ethyl-2,6-dinitrophenol (33)



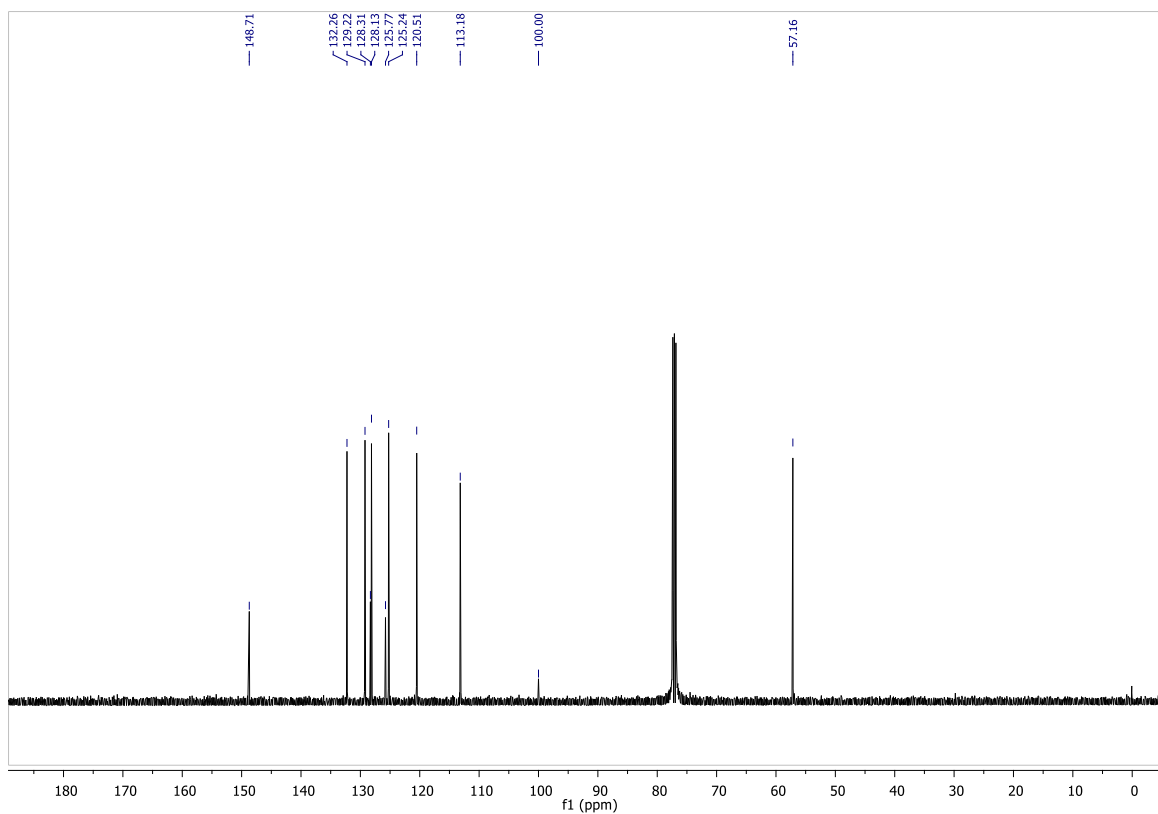
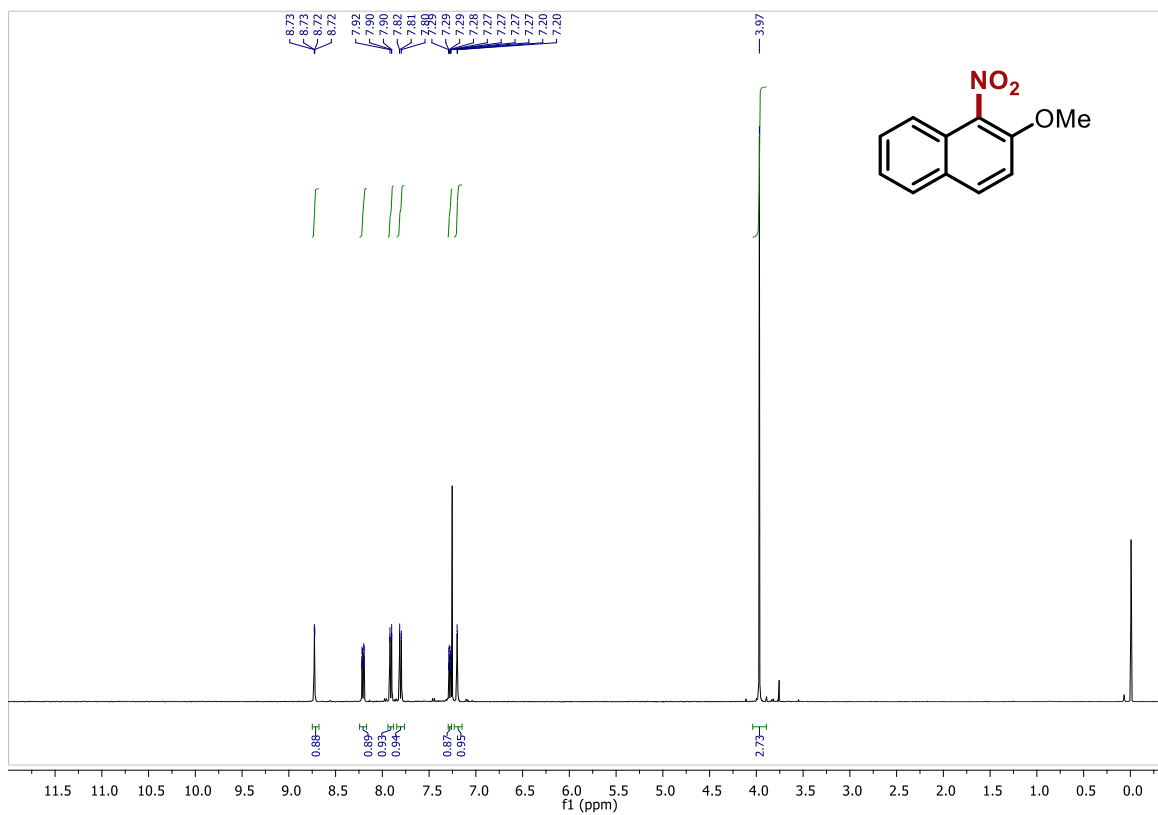
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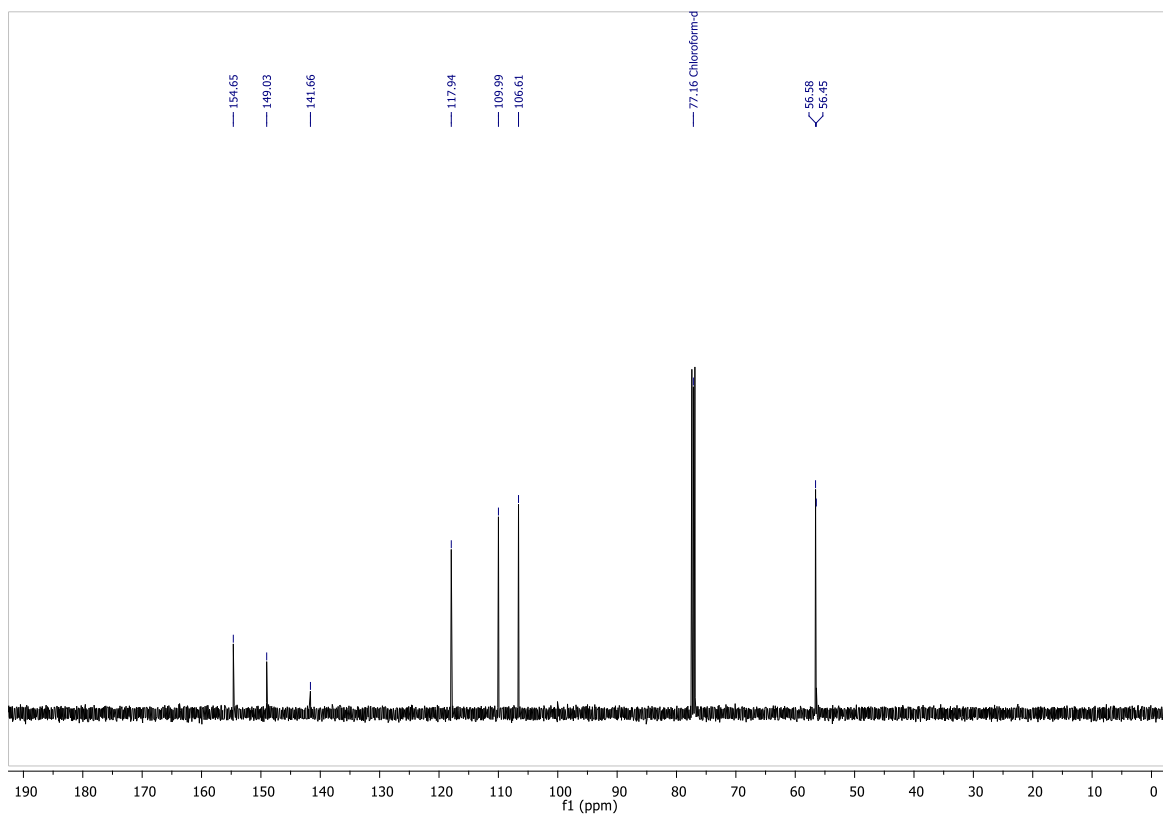
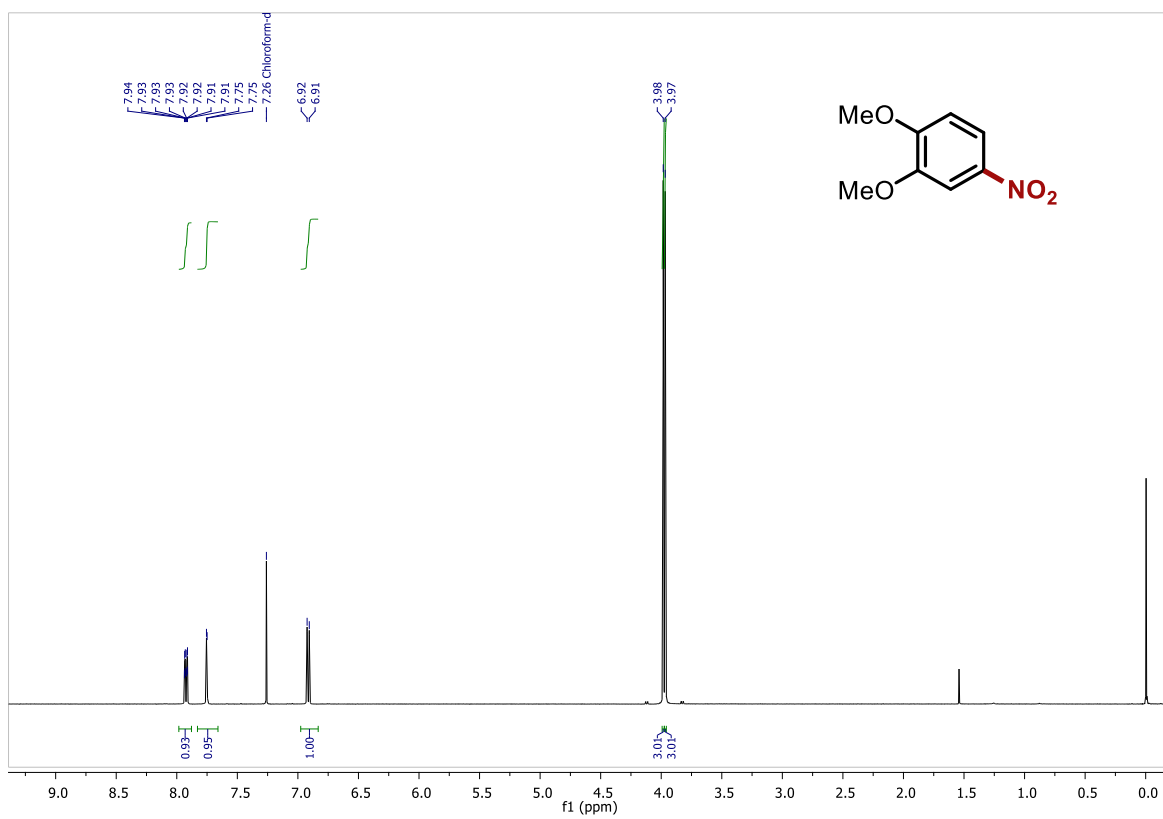
4-*tert*-butyl-2,6-dinitrophenol (35)



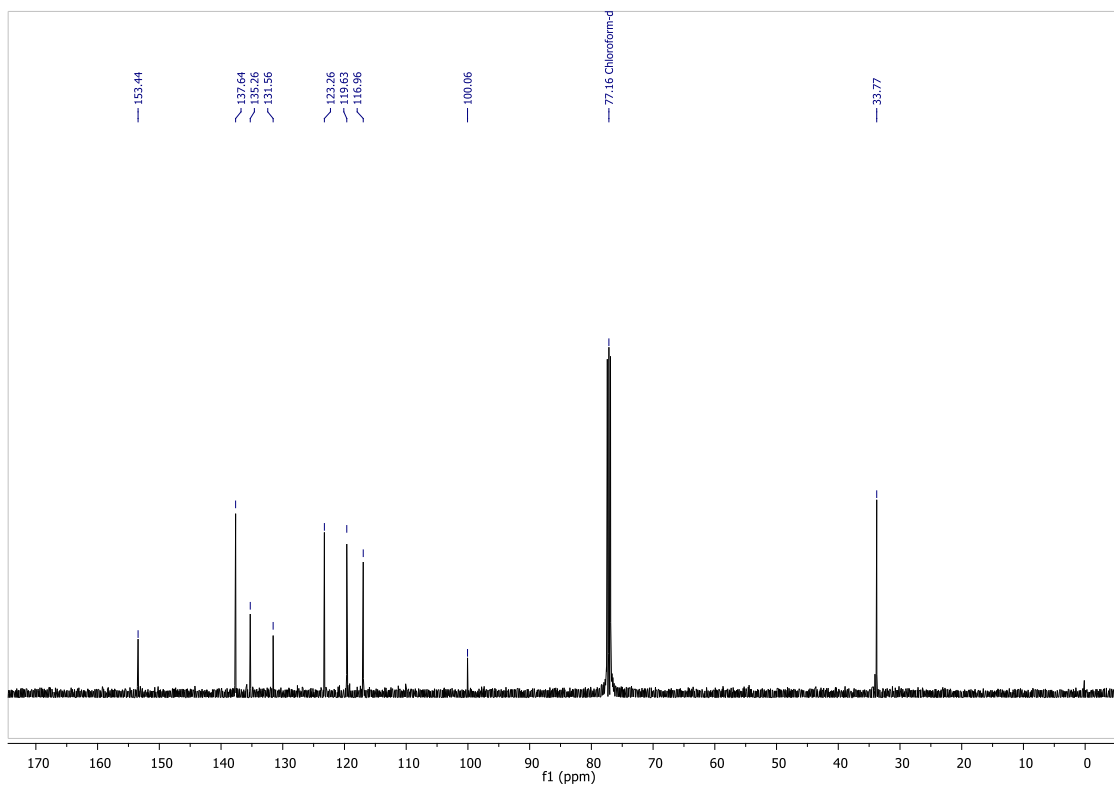
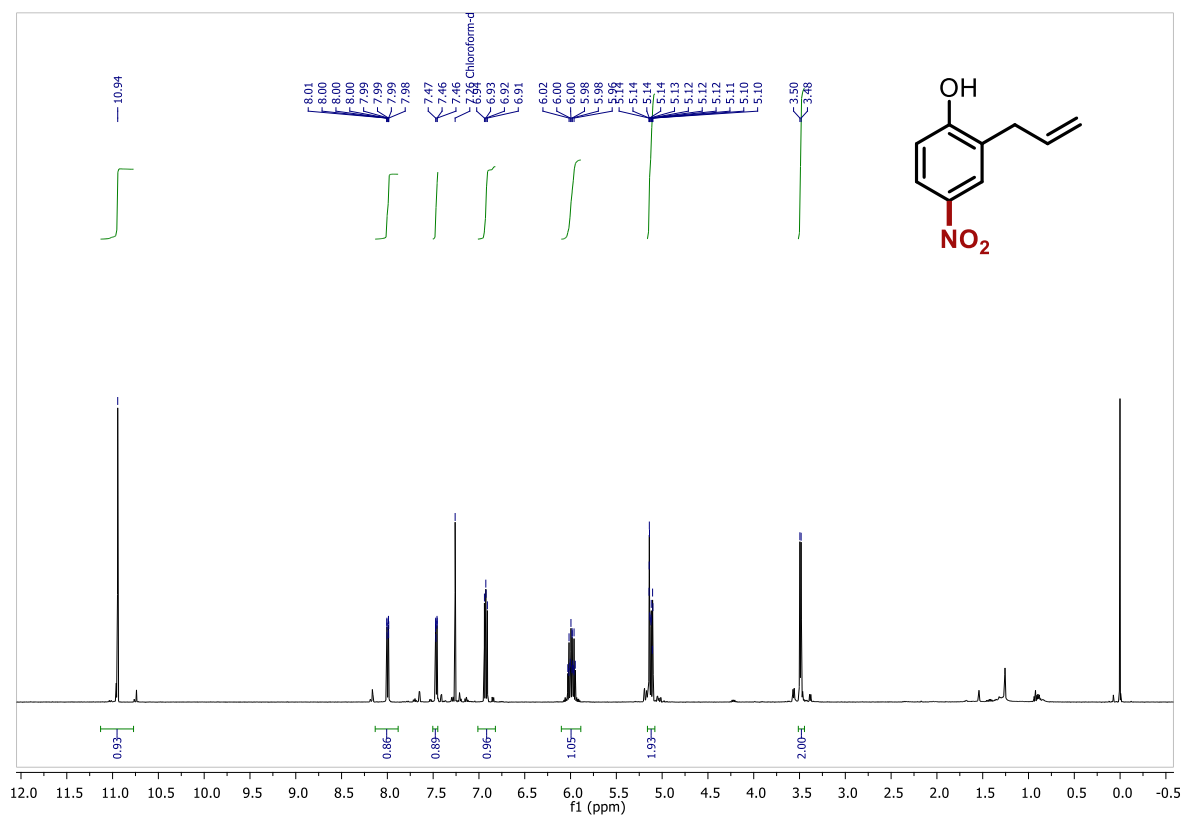
2-methoxy-1-nitronaphthalene (36)



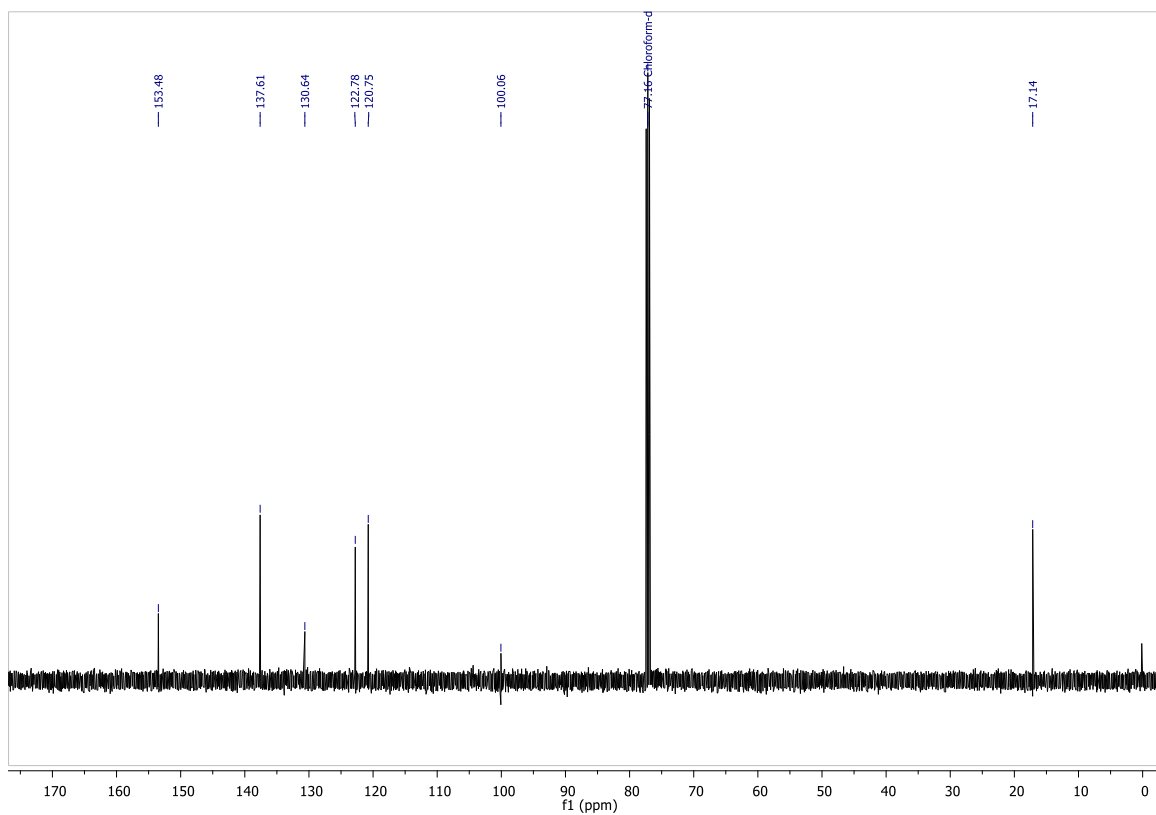
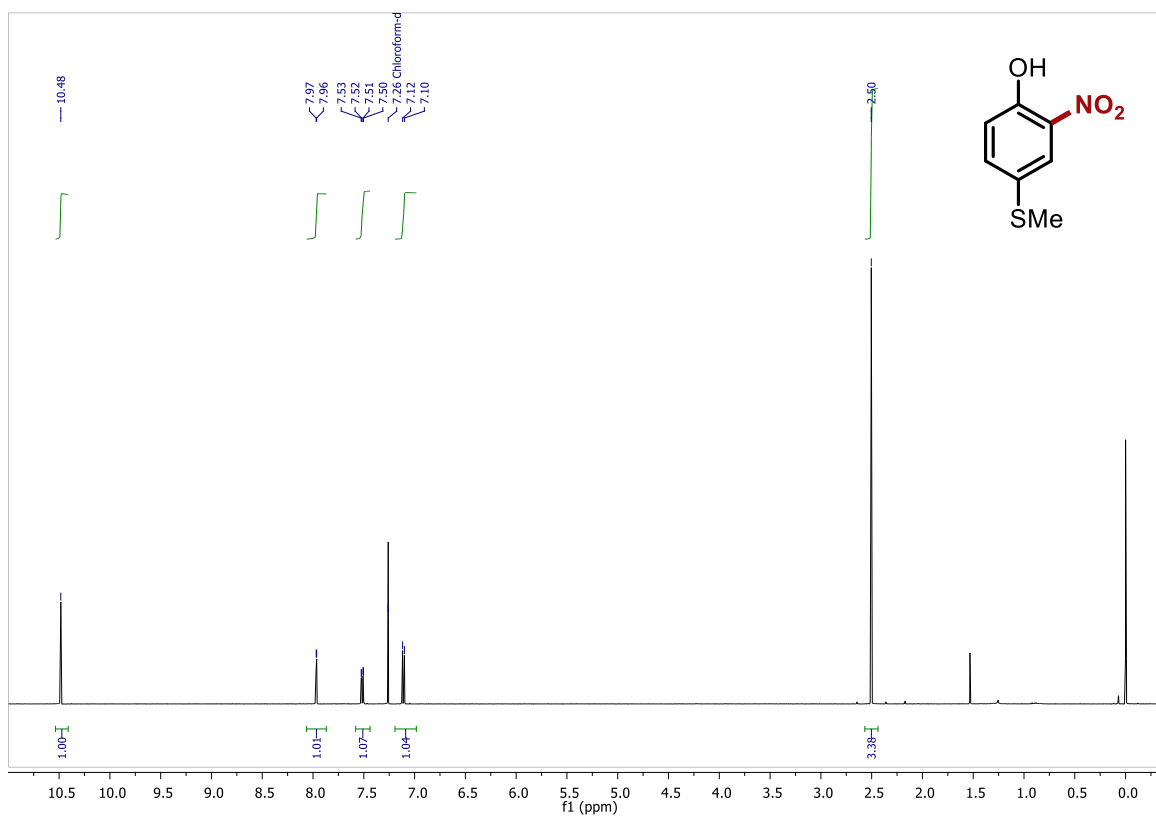
1,2-dimethoxy-4-nitrobenzene (37)



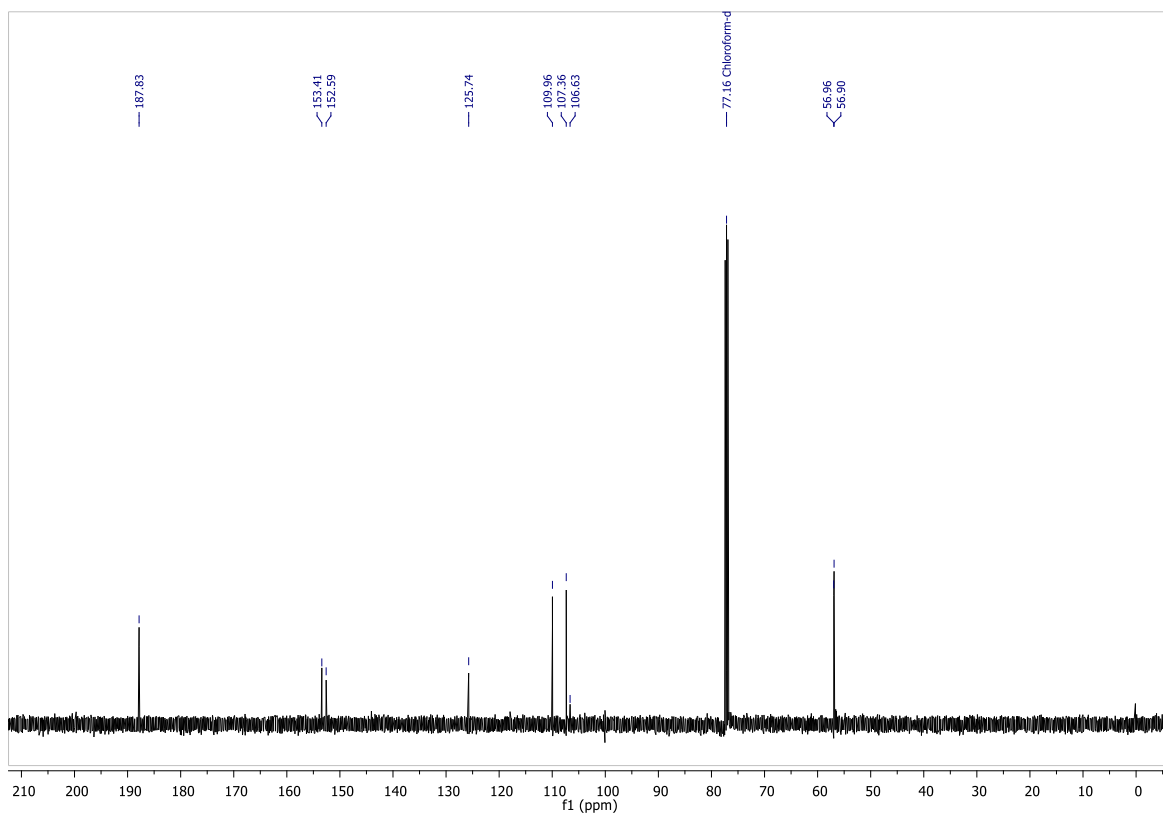
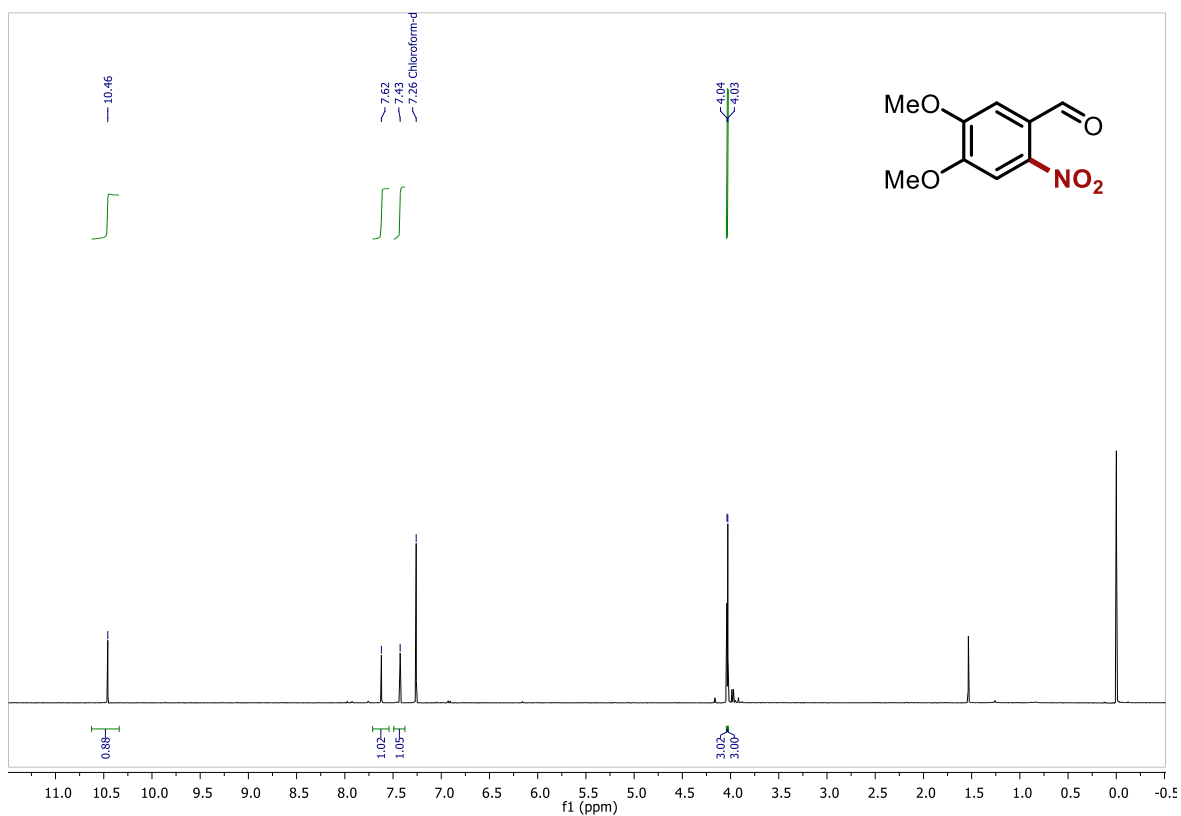
2-allyl-4-nitrophenol (38)



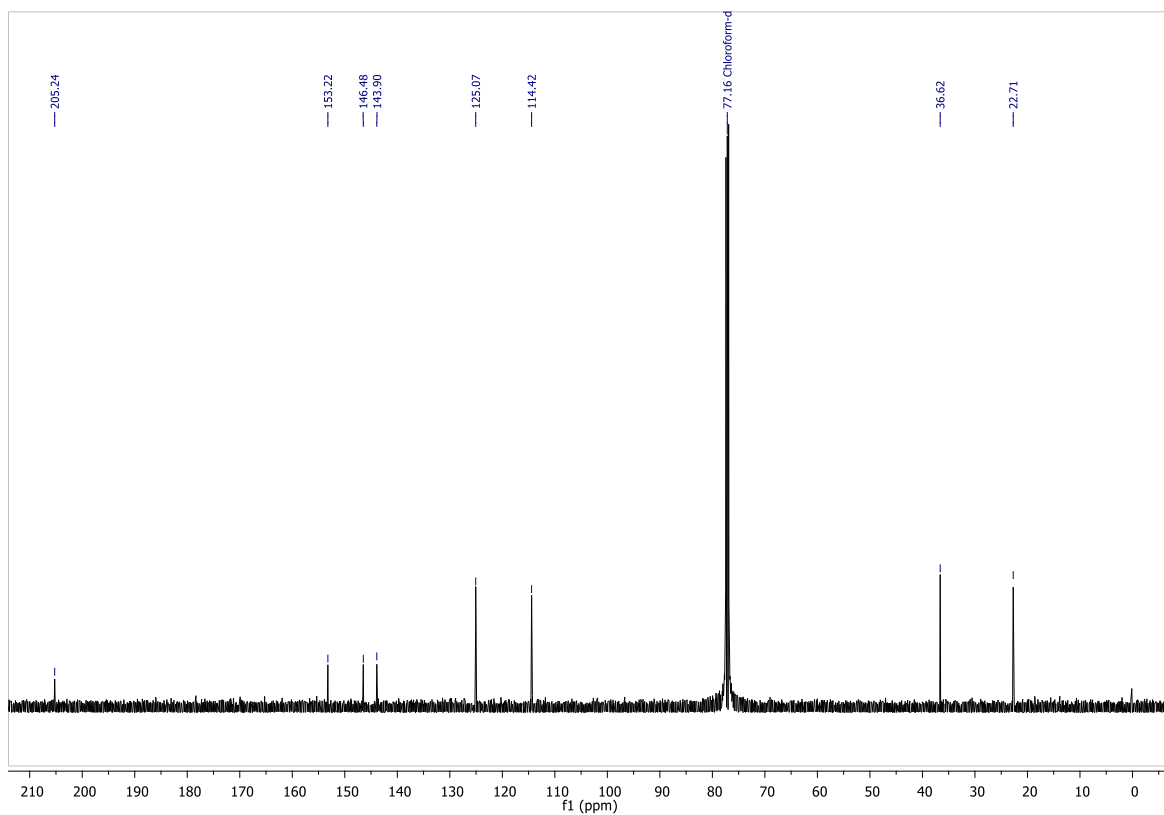
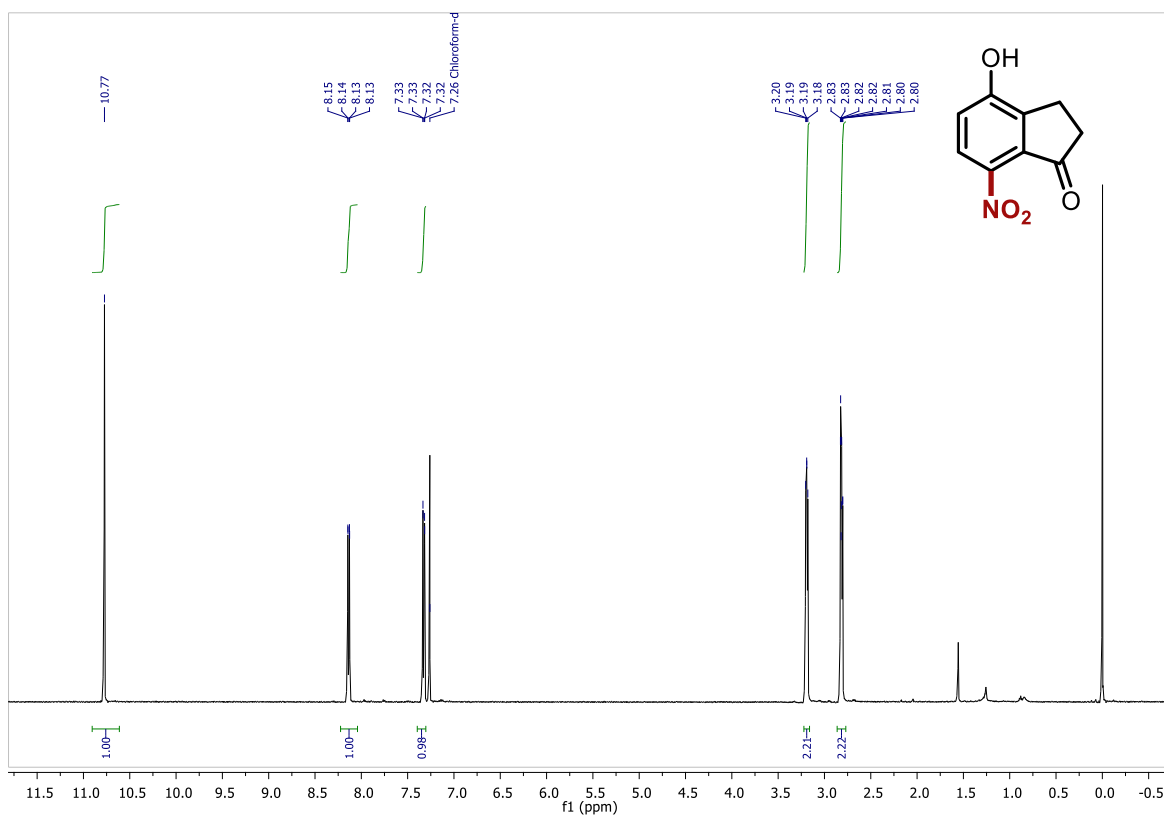
4-(methylthio)-2-nitrophenol (39)



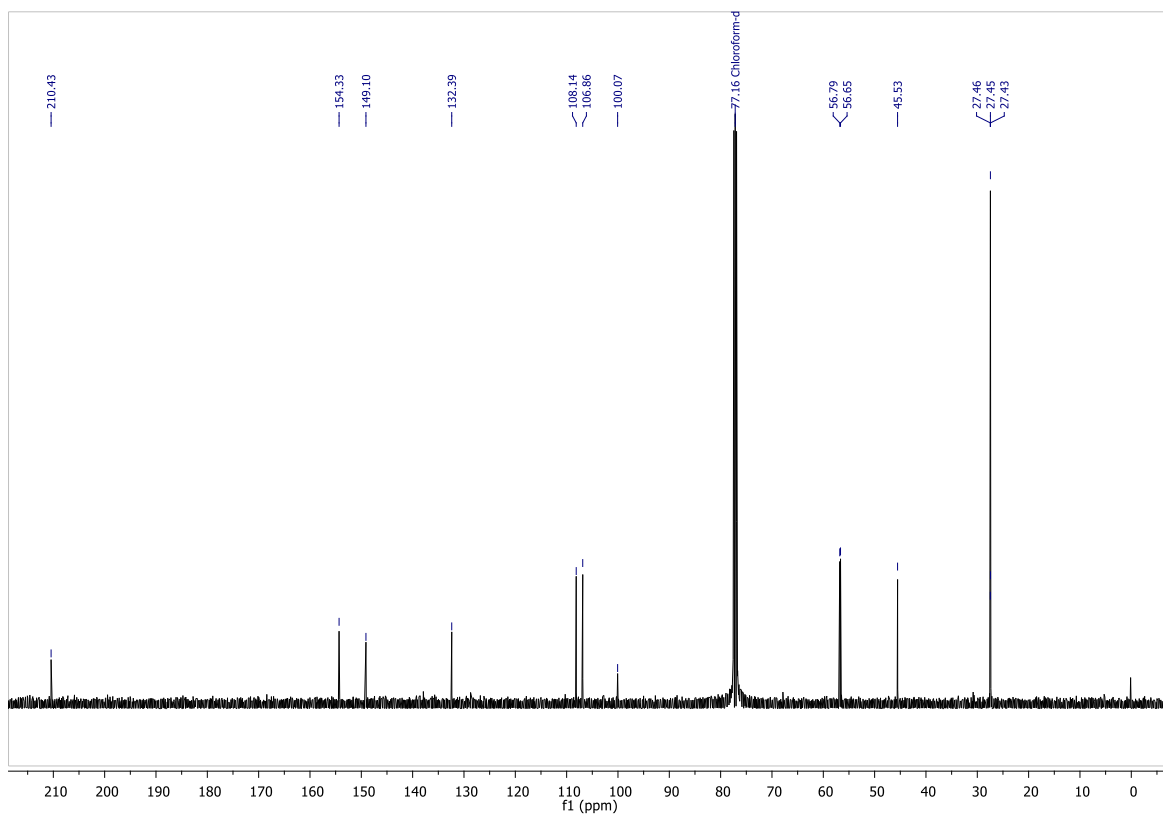
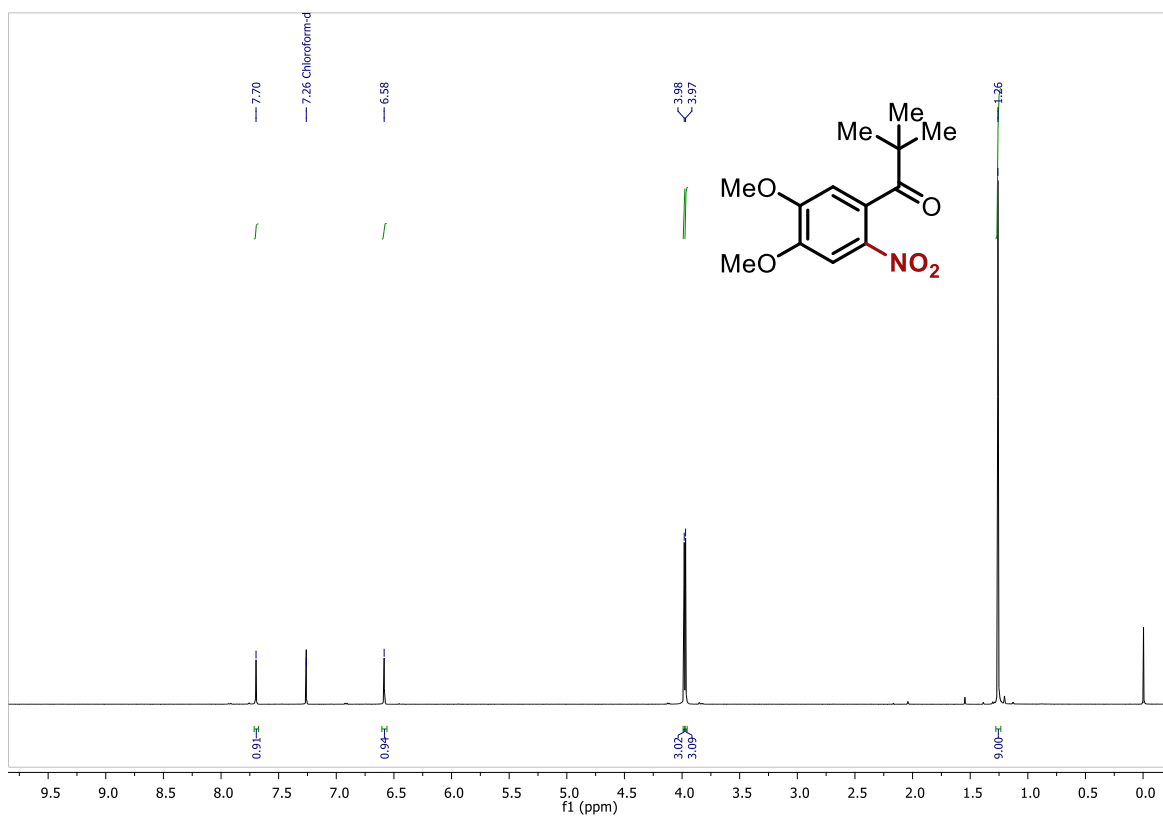
4,5-dimethoxy-2-nitrobenzaldehyde (40)



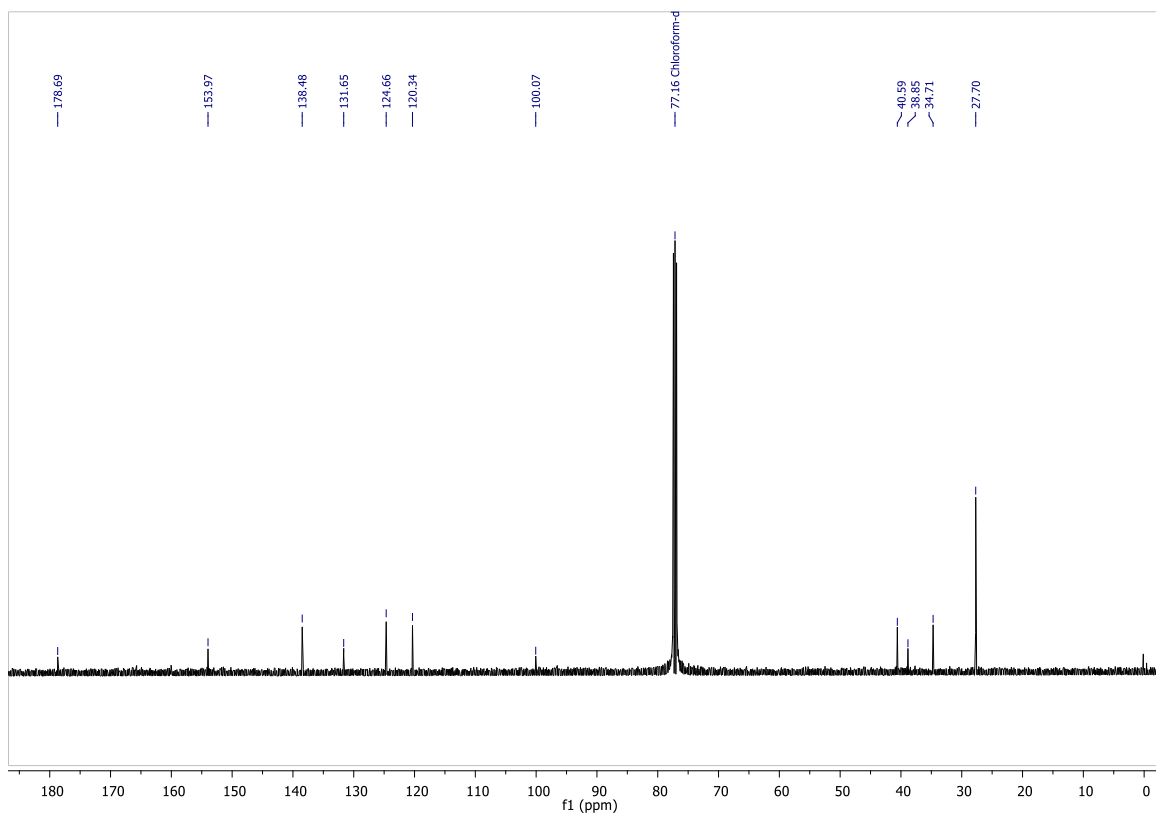
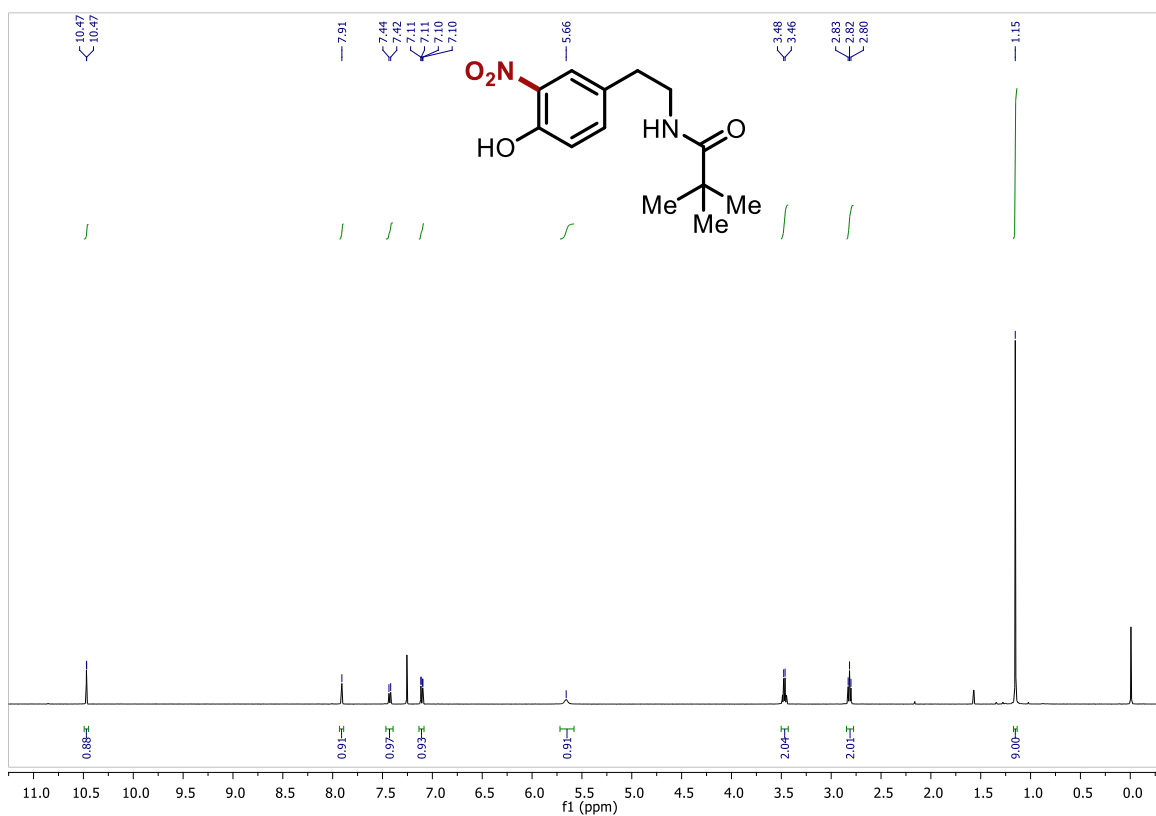
4-hydroxy-5-nitro-2,3-dihydro-1H-inden-1-one (41)



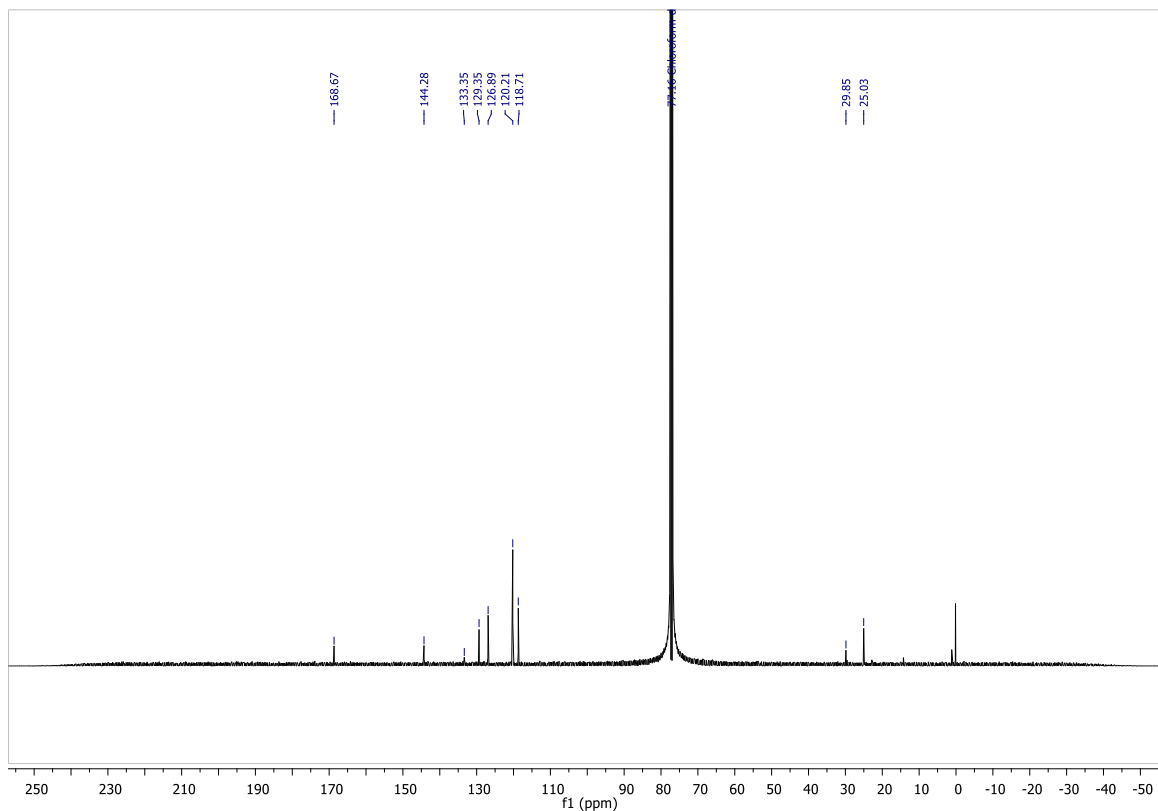
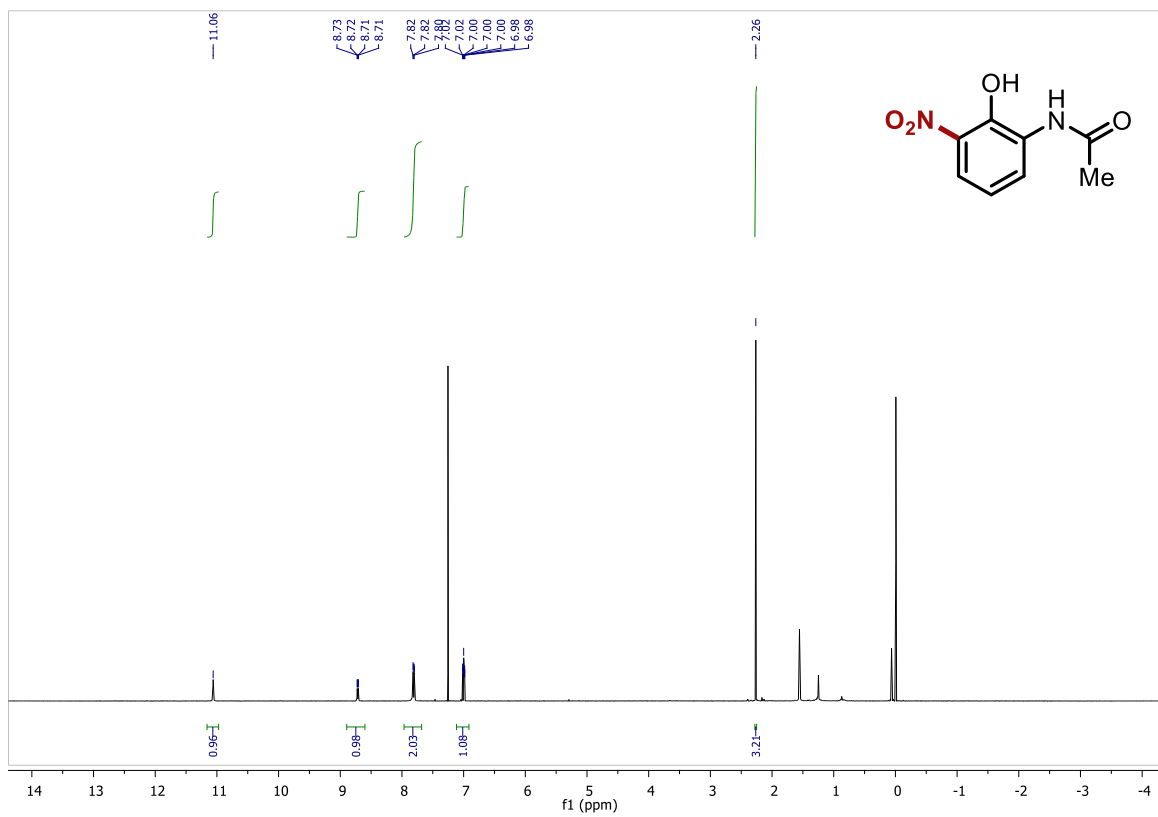
1-(4,5-dimethoxy-2-nitrophenyl)-2,2-dimethylpropan-1-one (42)



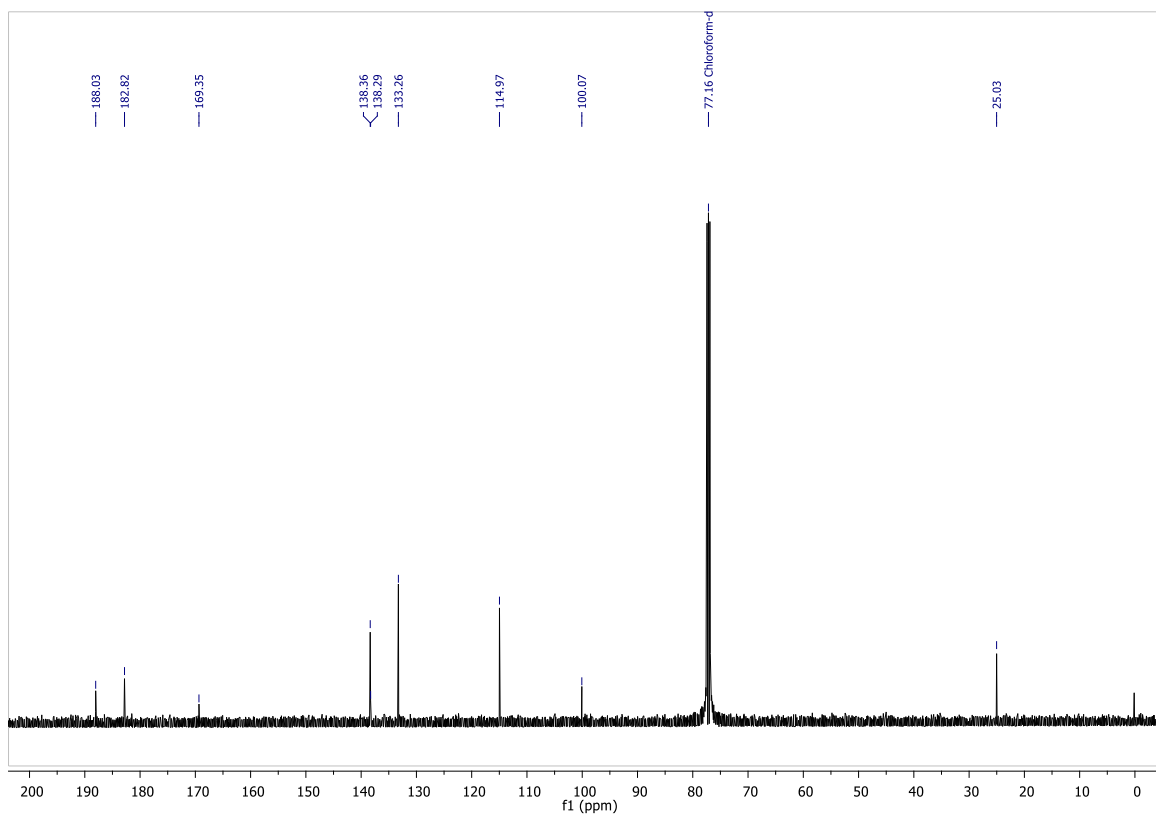
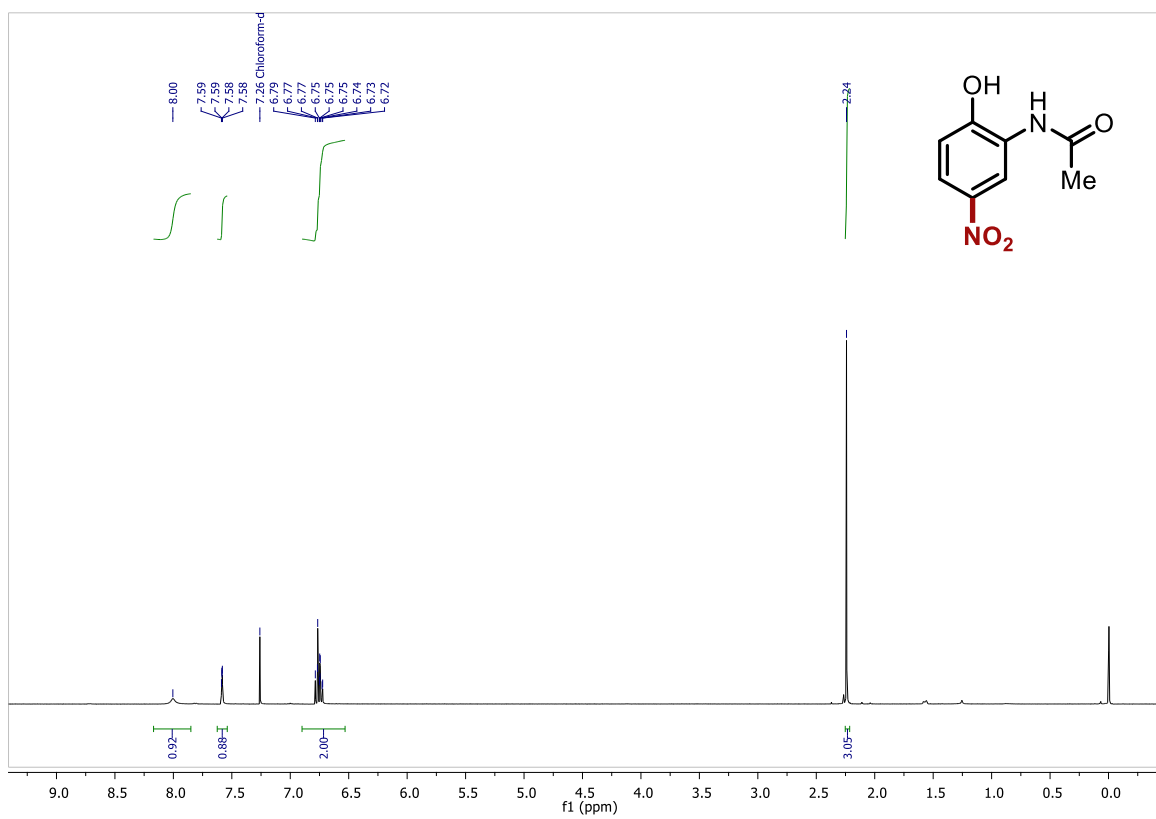
N-(Pivaloyl)-3-nitro-tyramine (43)



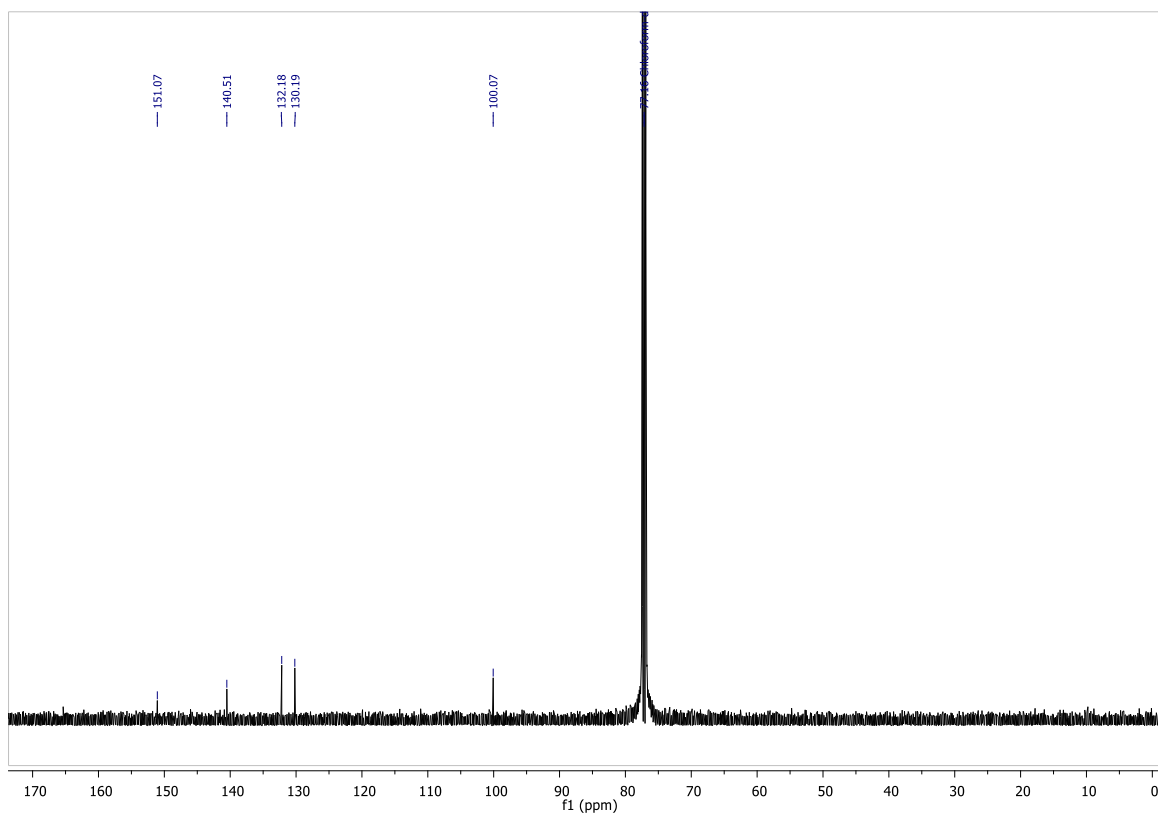
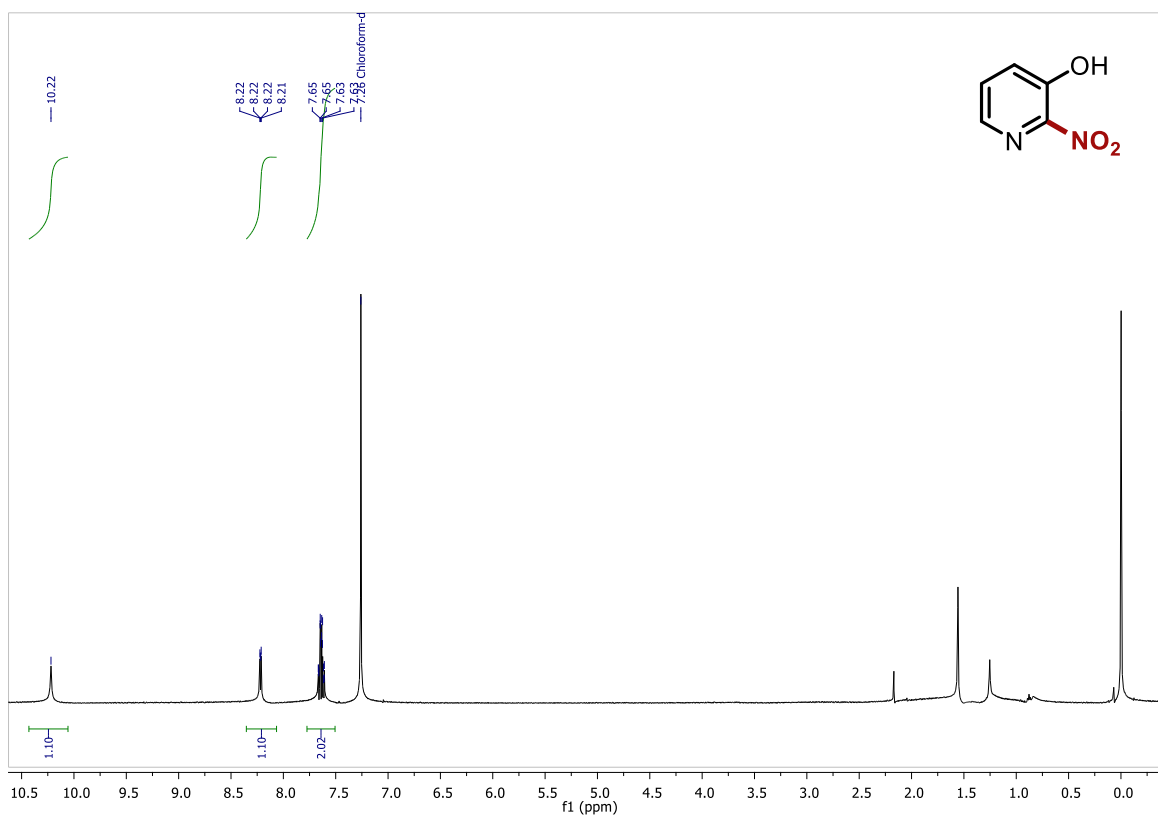
N-(2-hydroxy-6-nitrophenyl)acetamide (44)



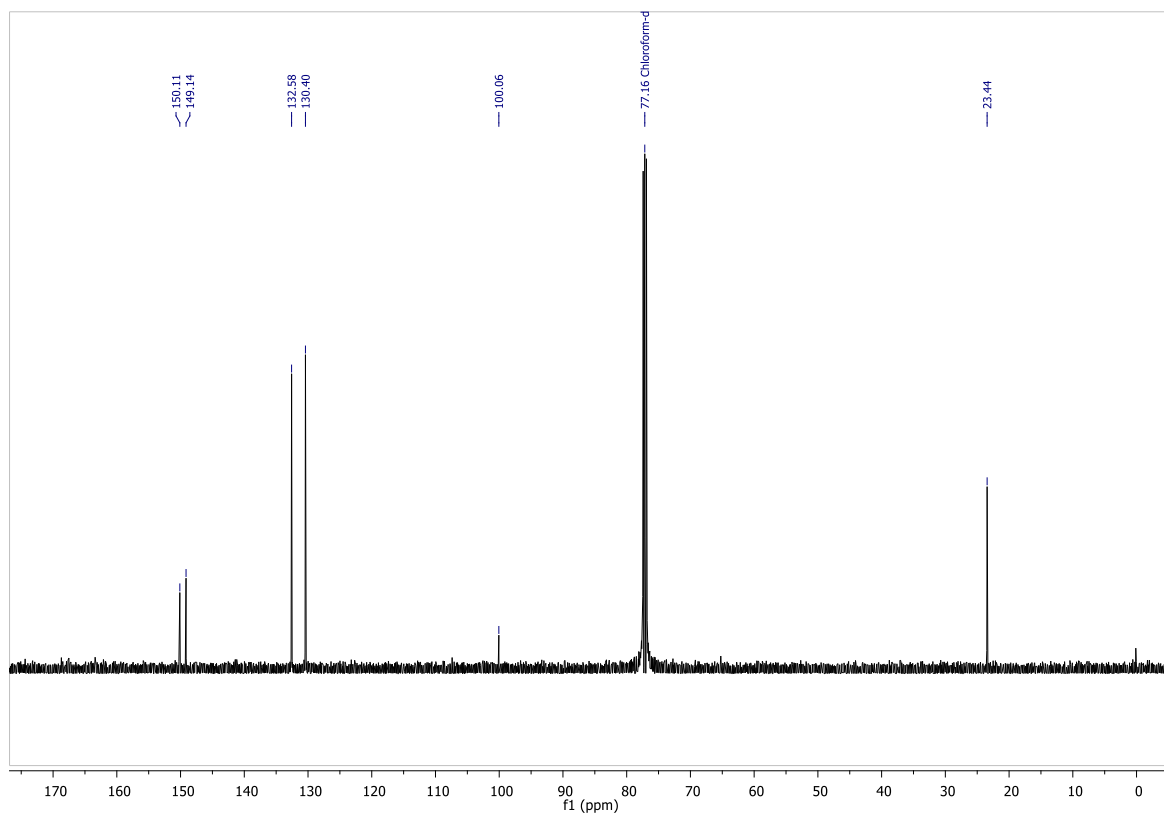
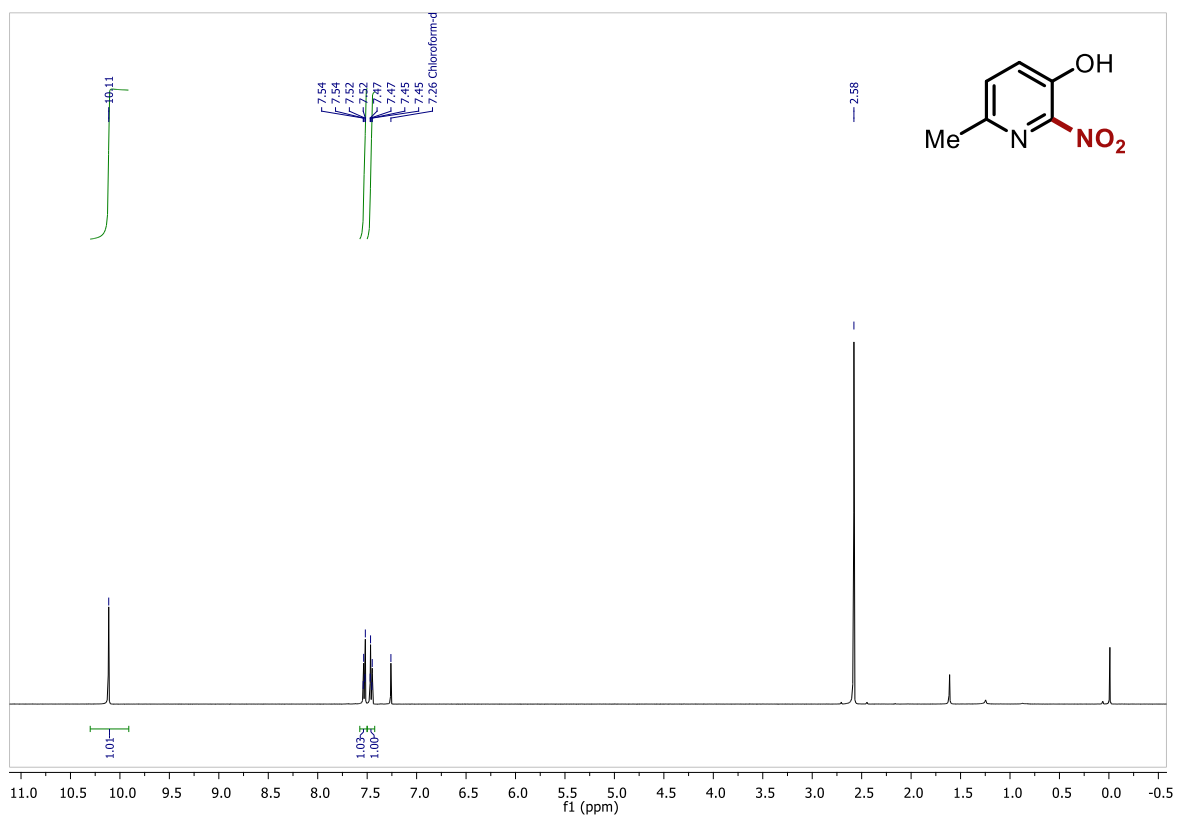
N-(2-hydroxy-3-nitrophenyl)acetamide (45)



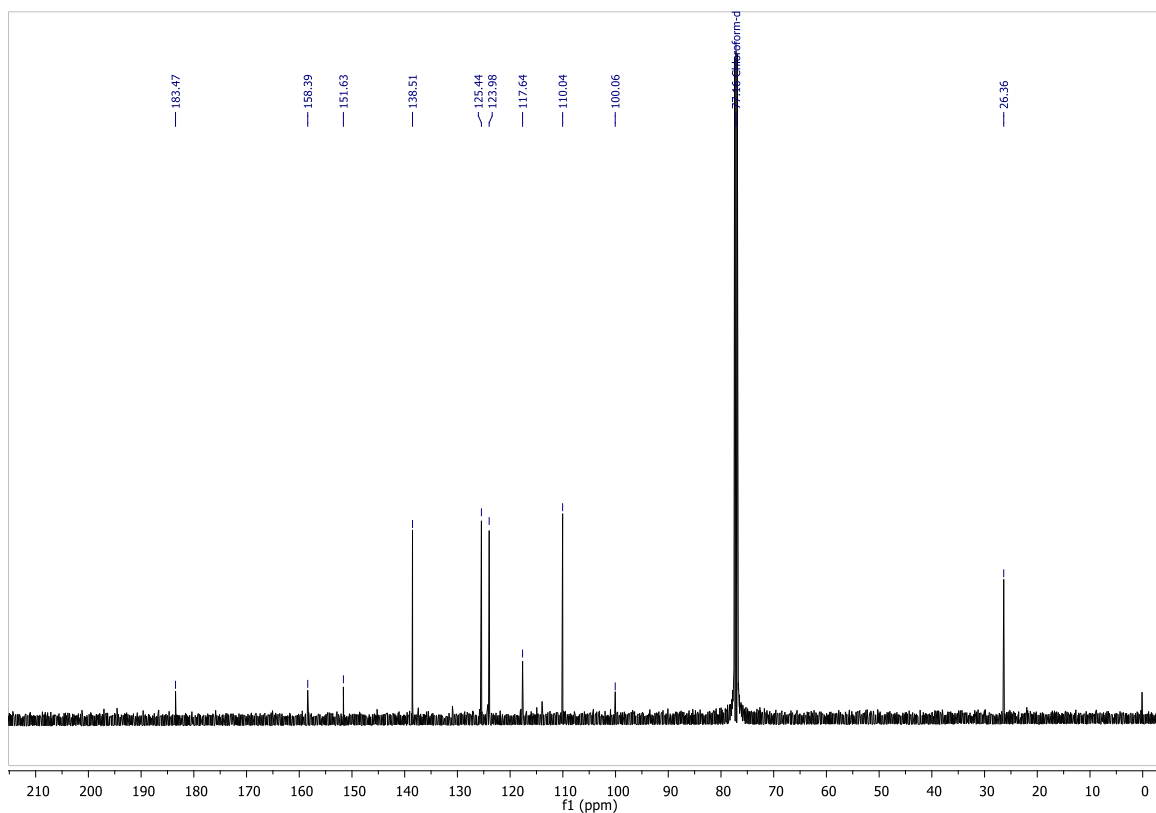
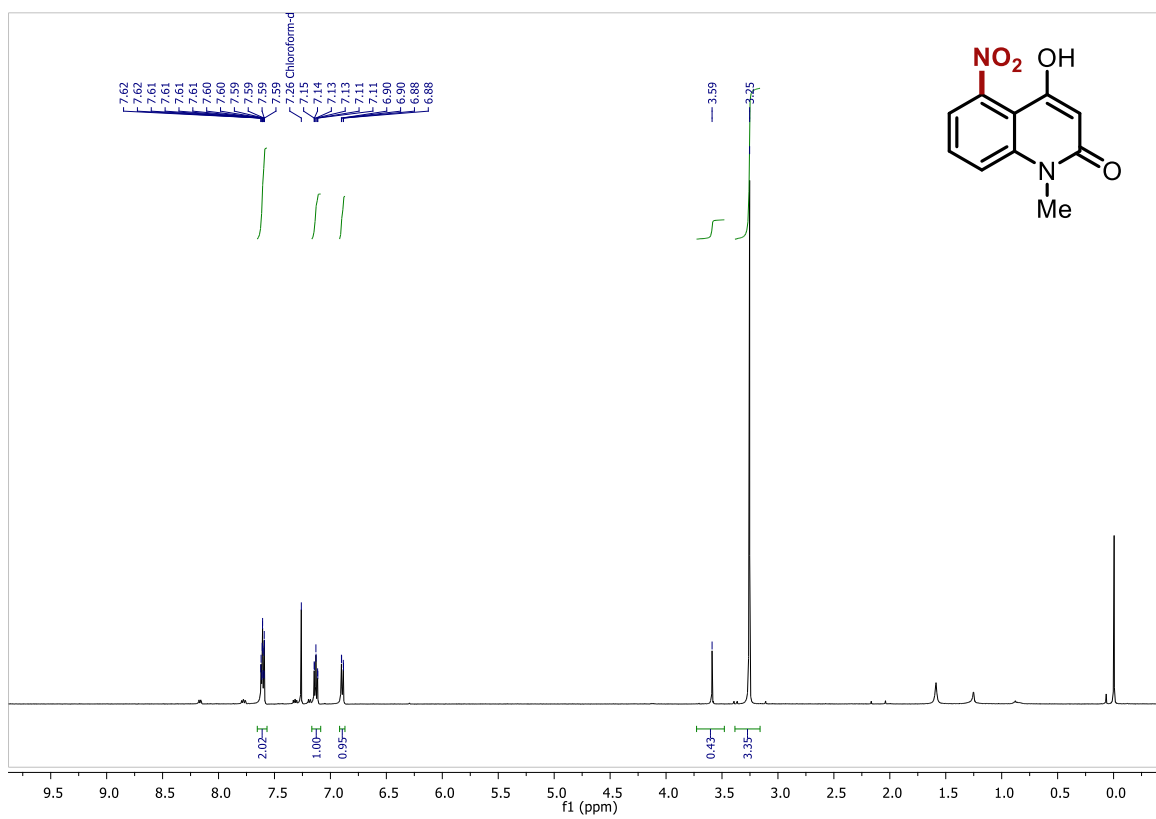
2-nitropyridin-3-ol (46)



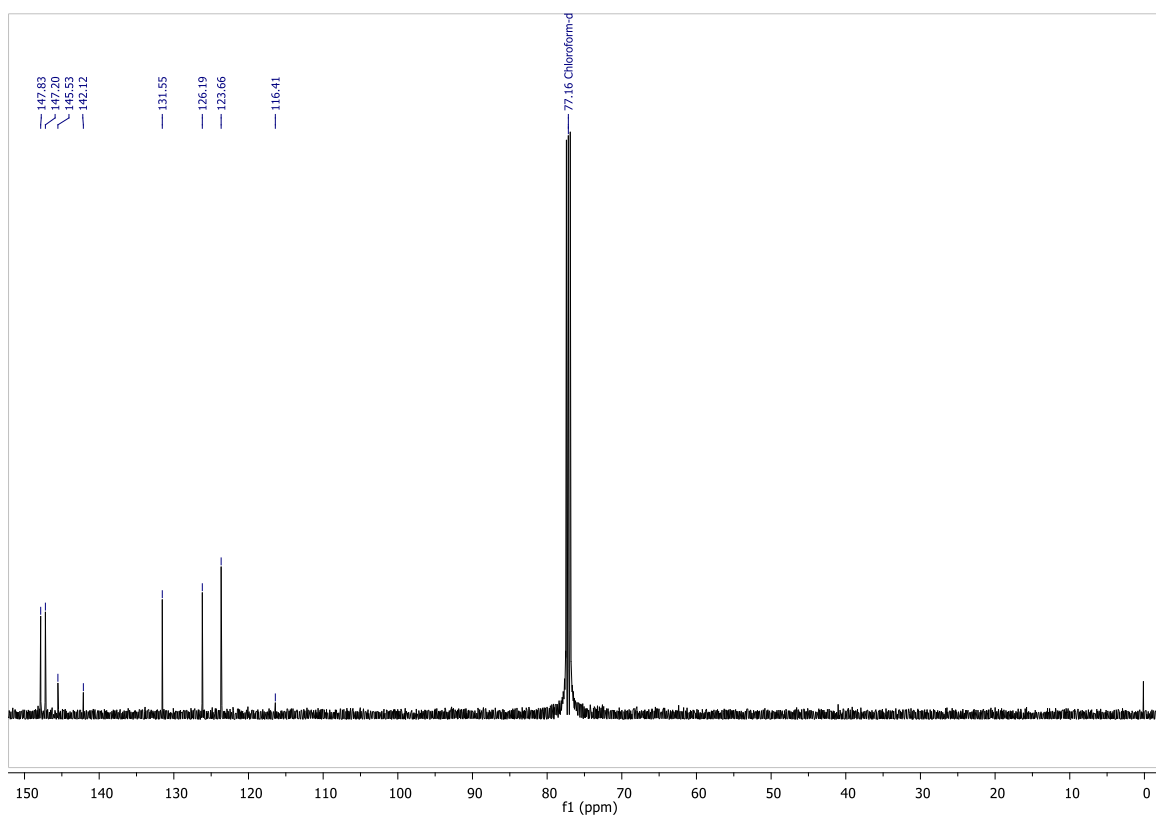
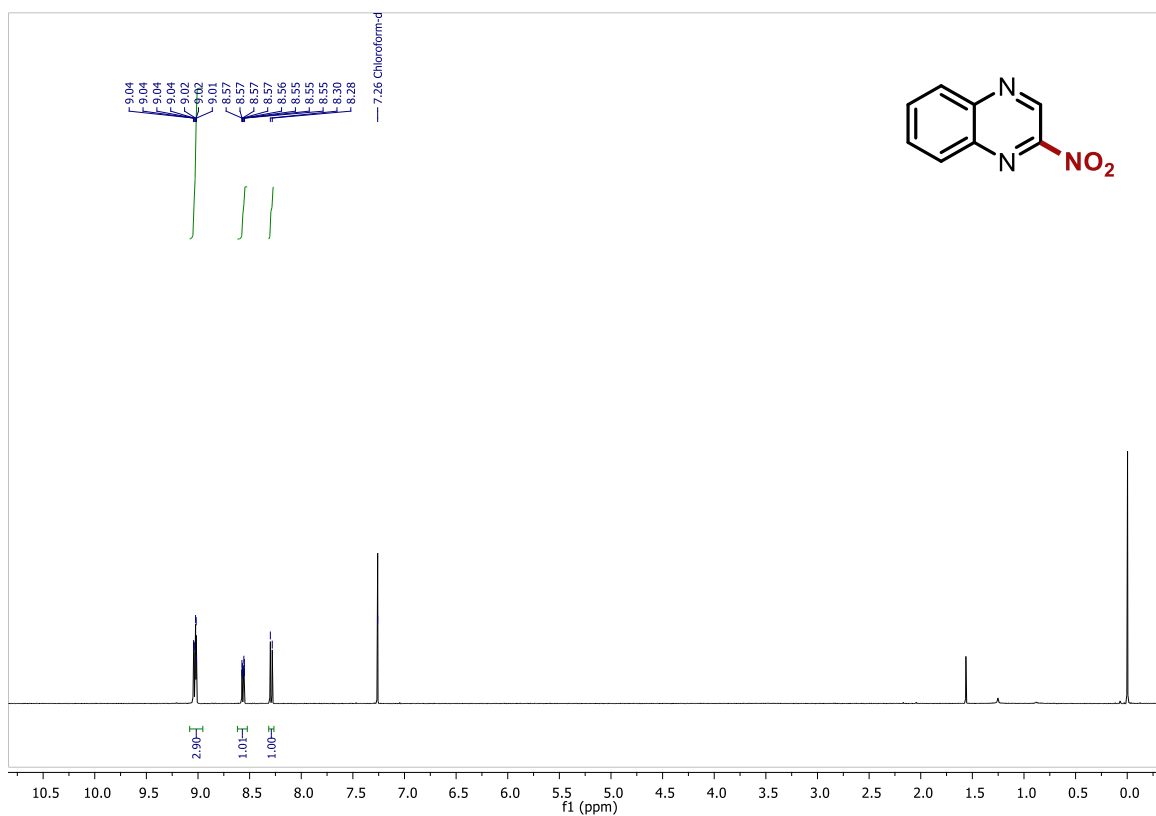
6-methyl-2-nitropyridin-3-ol (47)



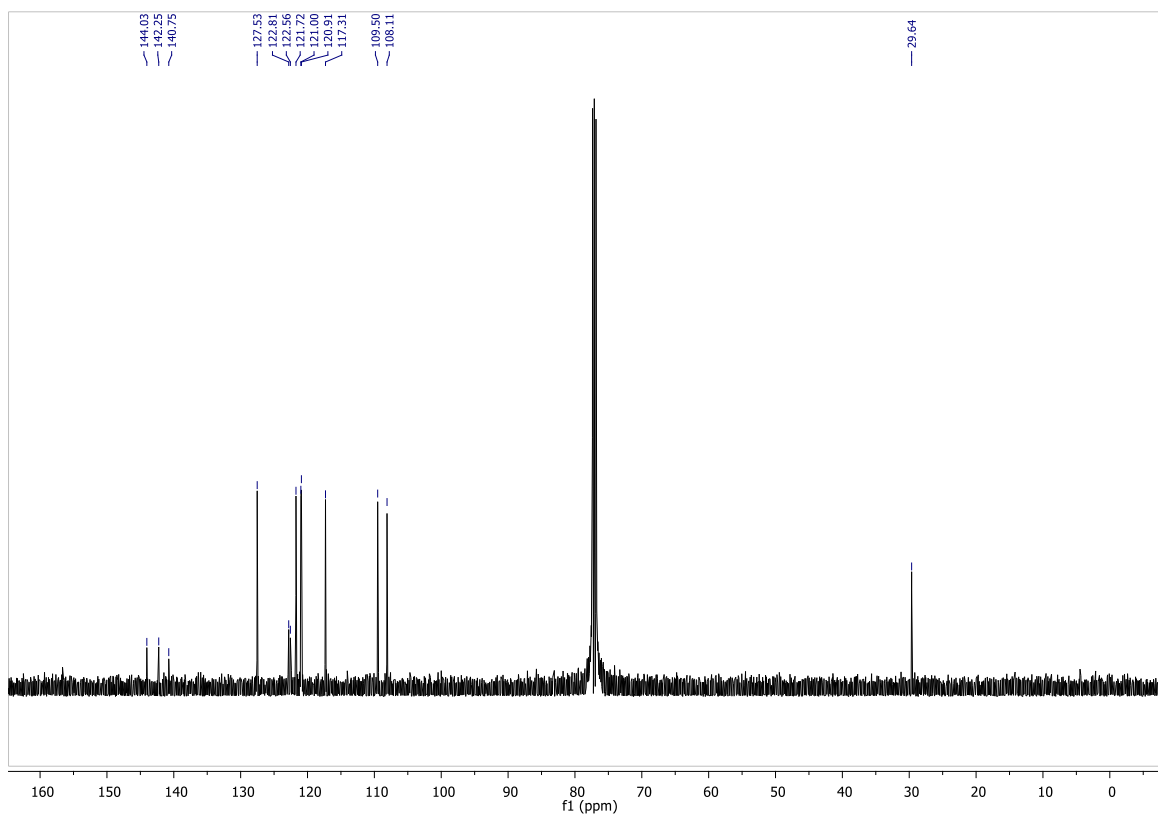
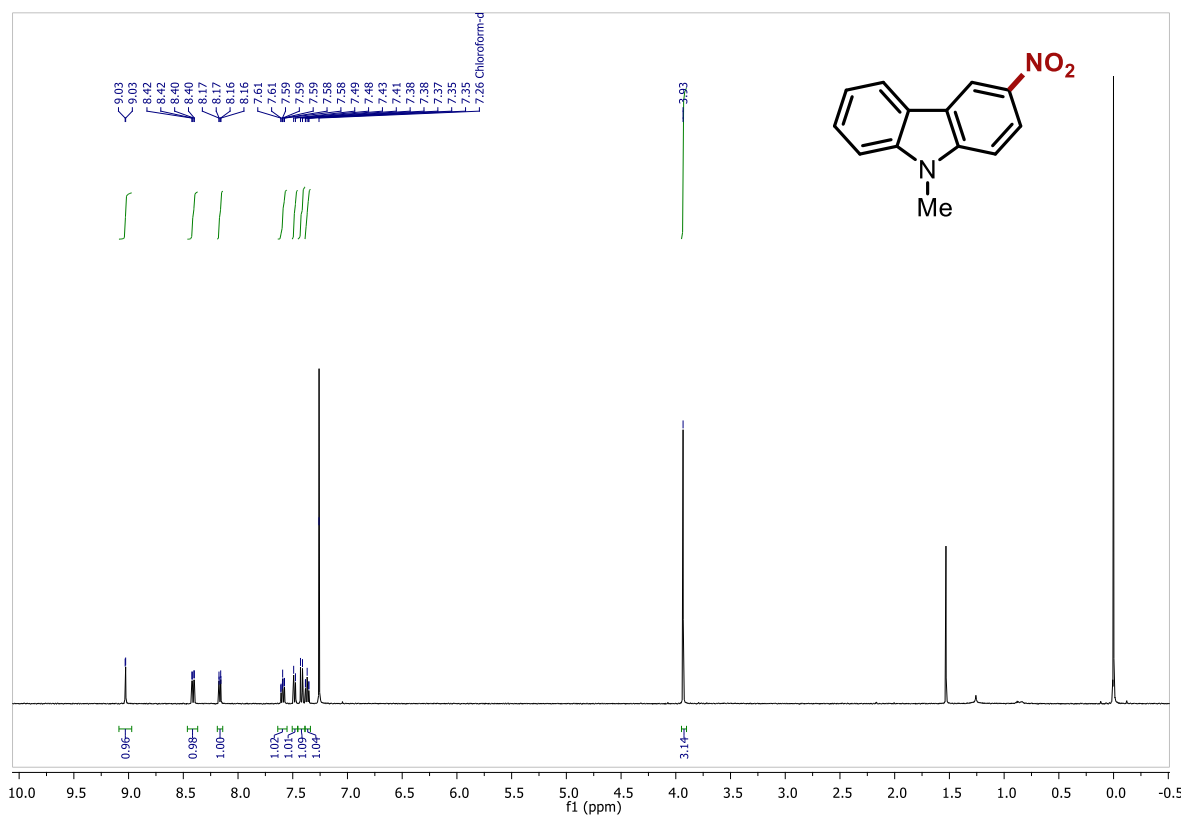
4-hydroxy-1-methyl-5-nitroquinolin-2(1H)-one (48)



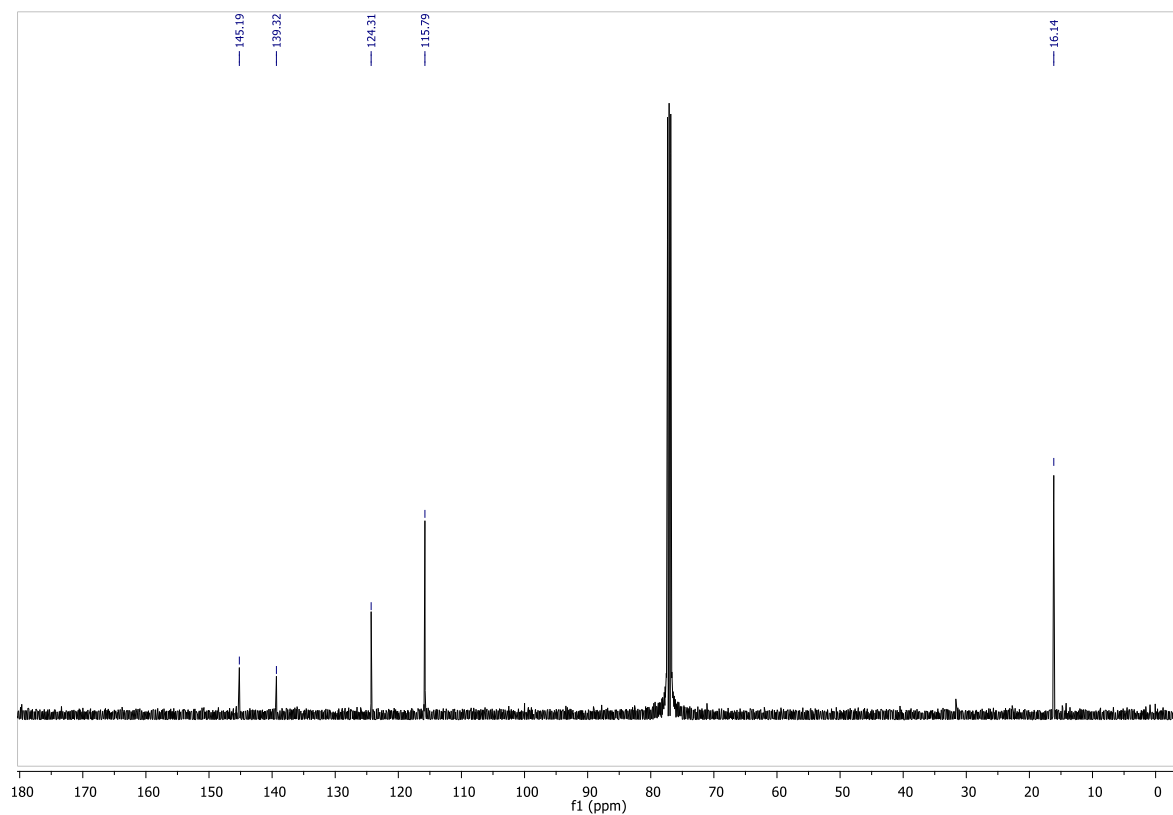
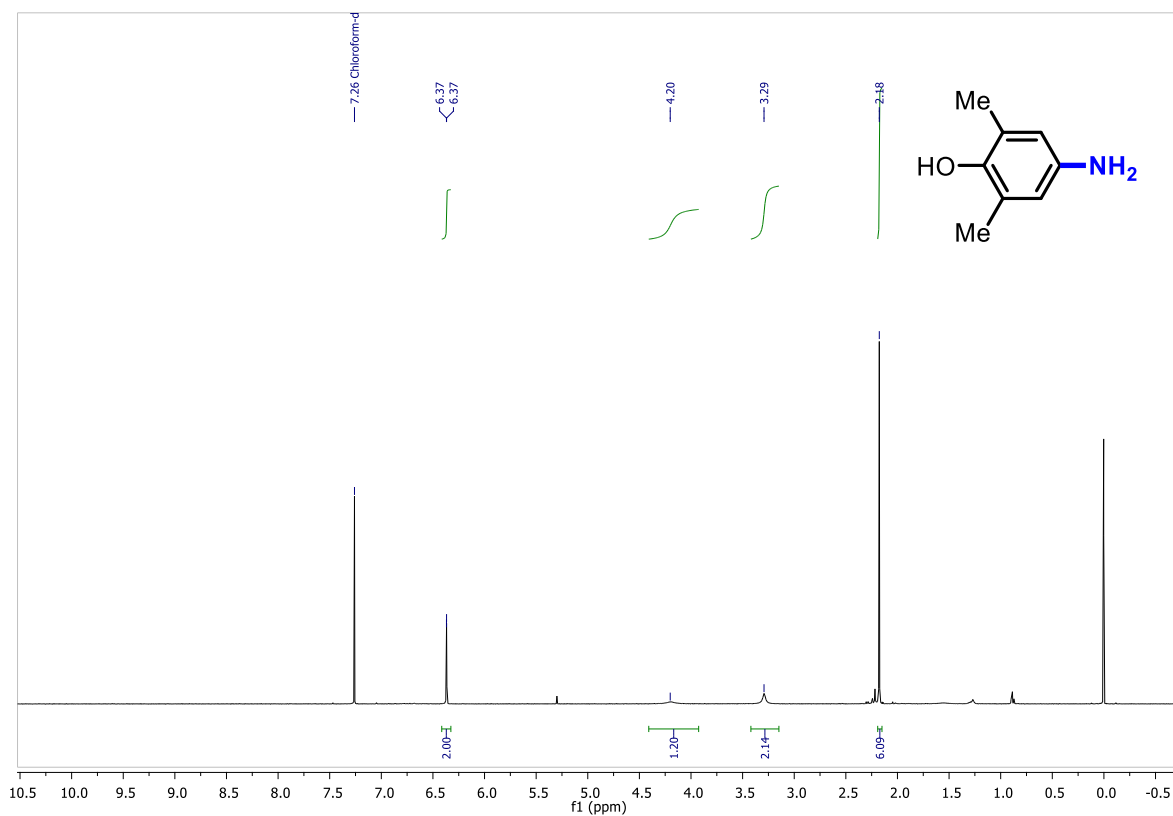
2-nitroquinoxaline (49)



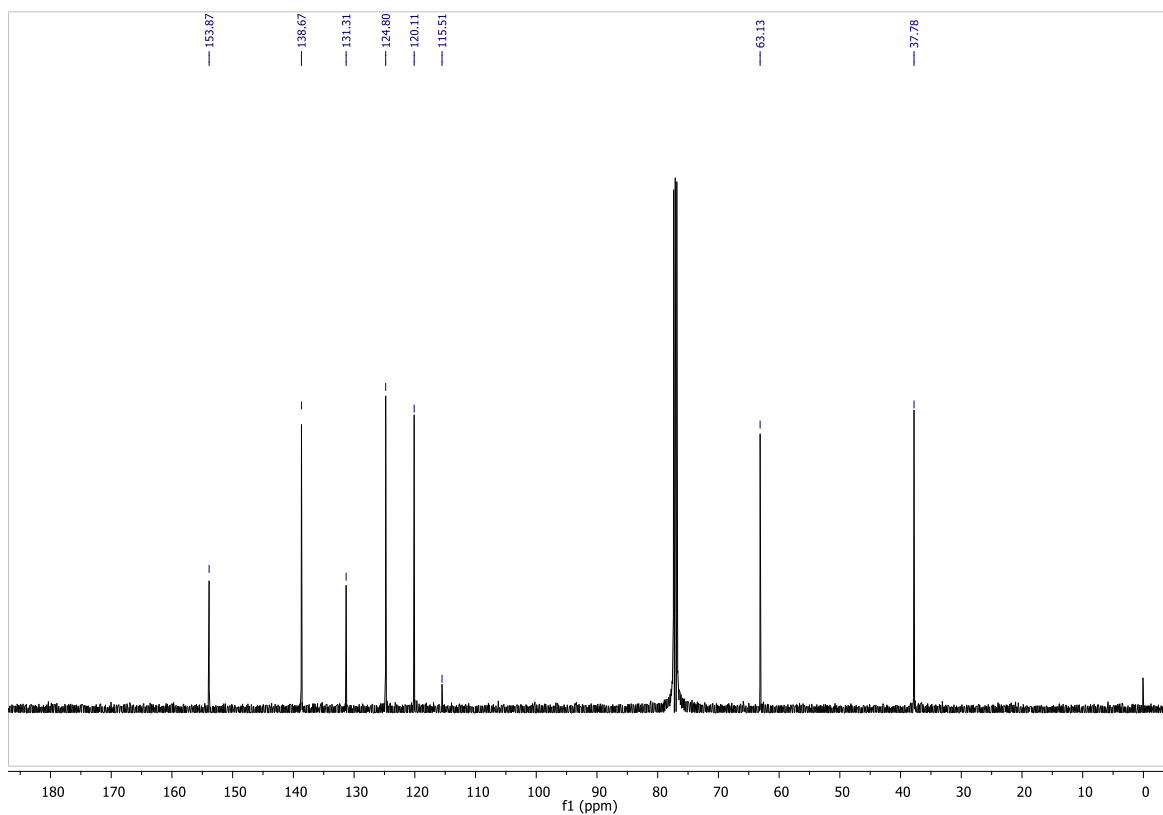
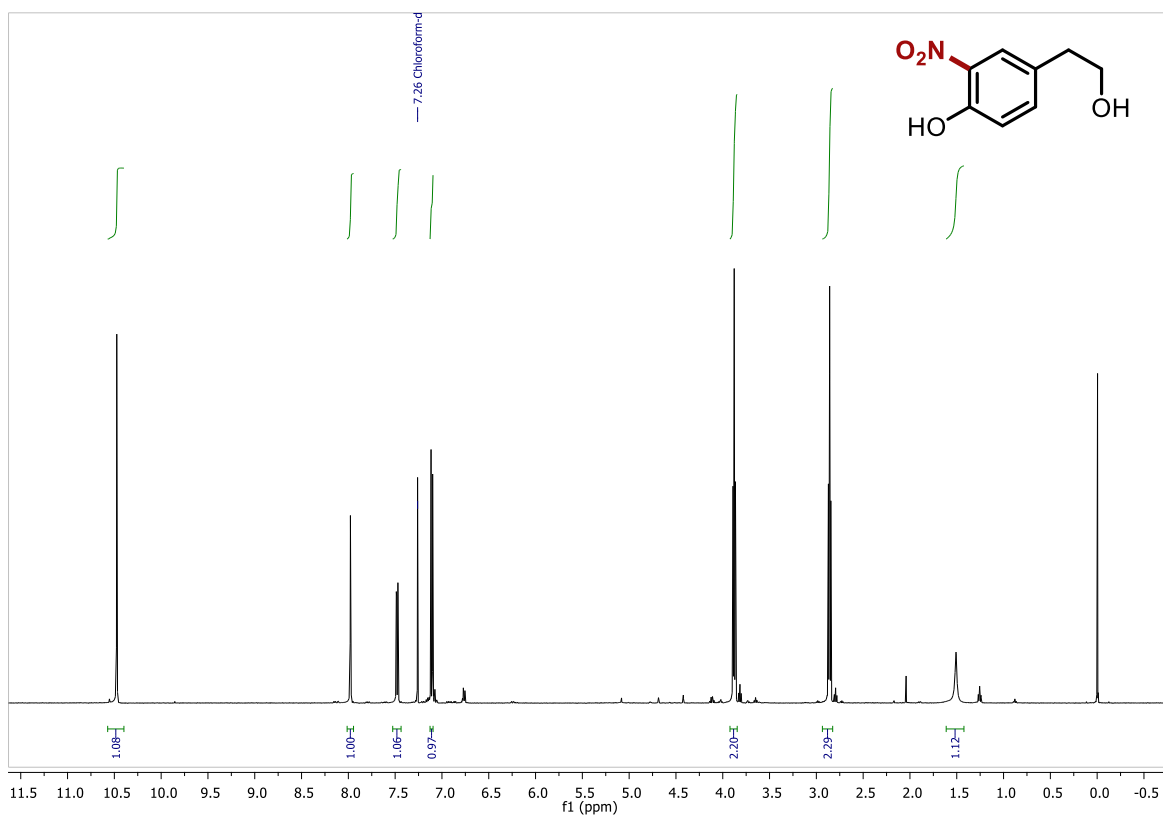
9-methyl-3-nitrocarbazole (50).



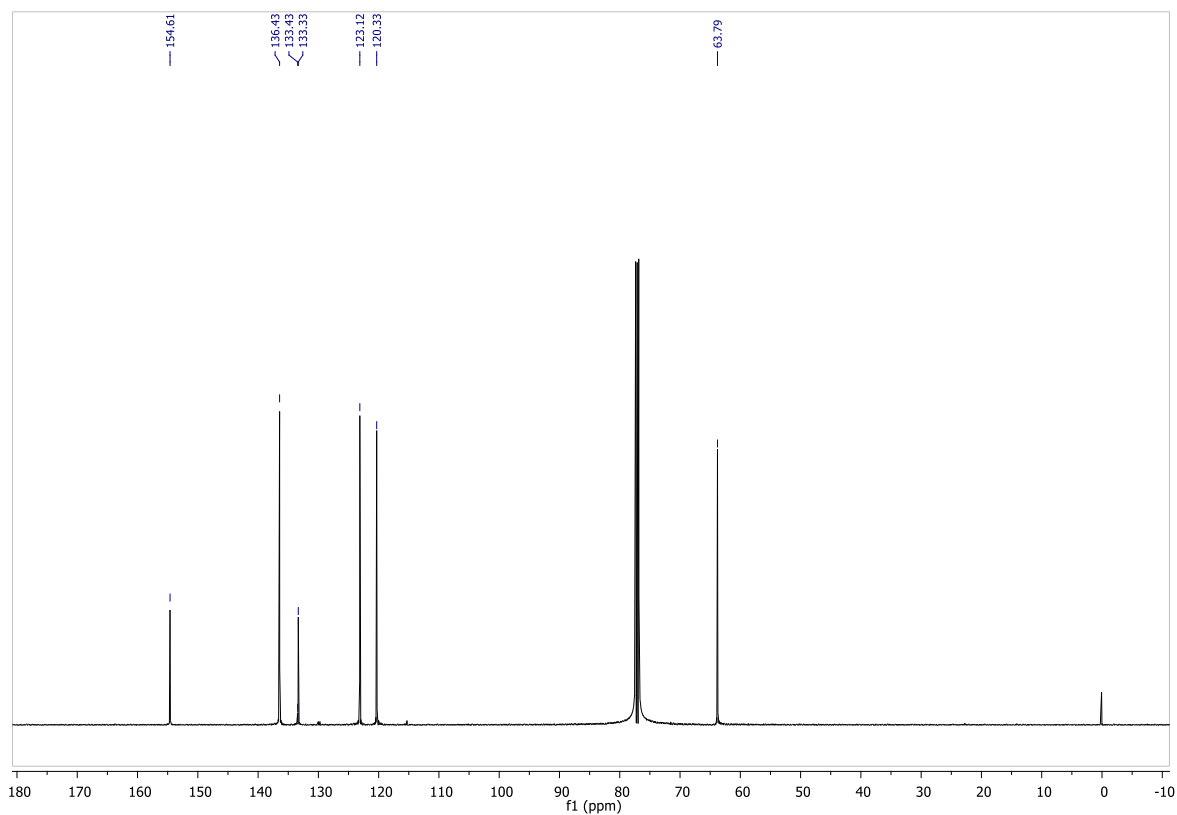
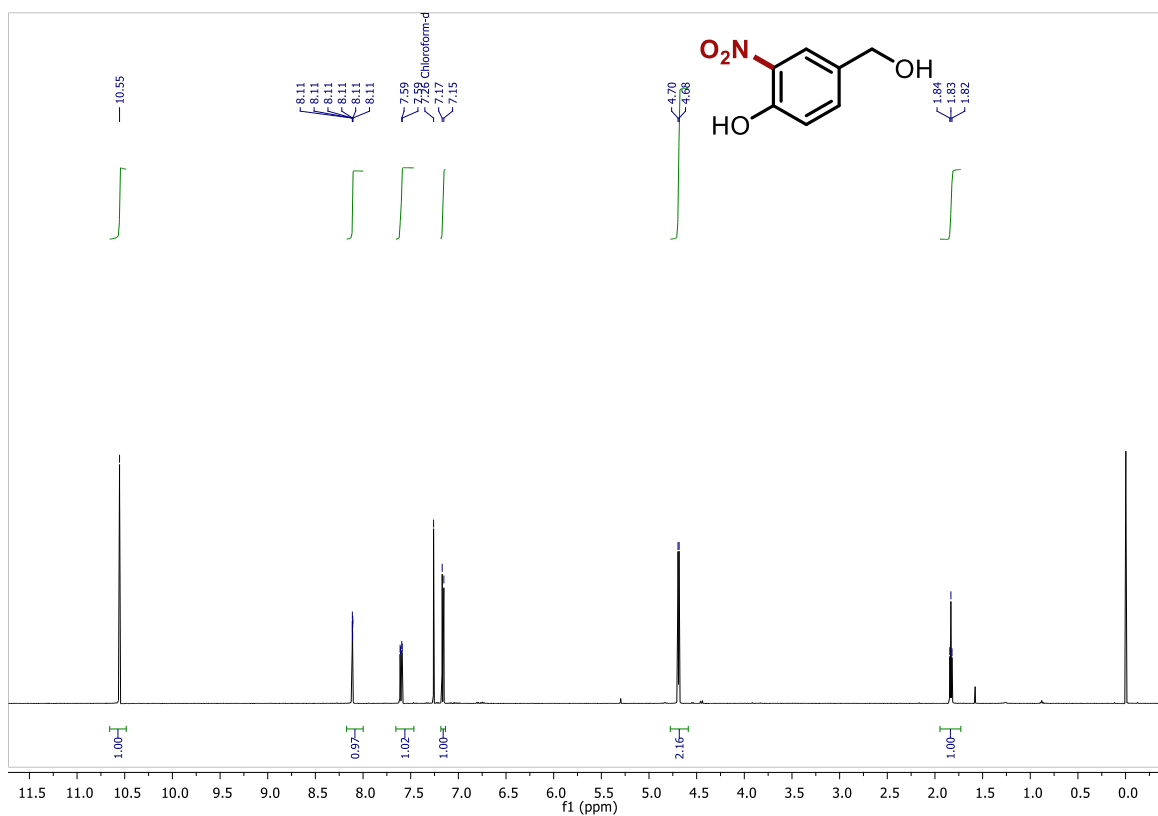
4-amino-2,6-dimethylphenol (51)



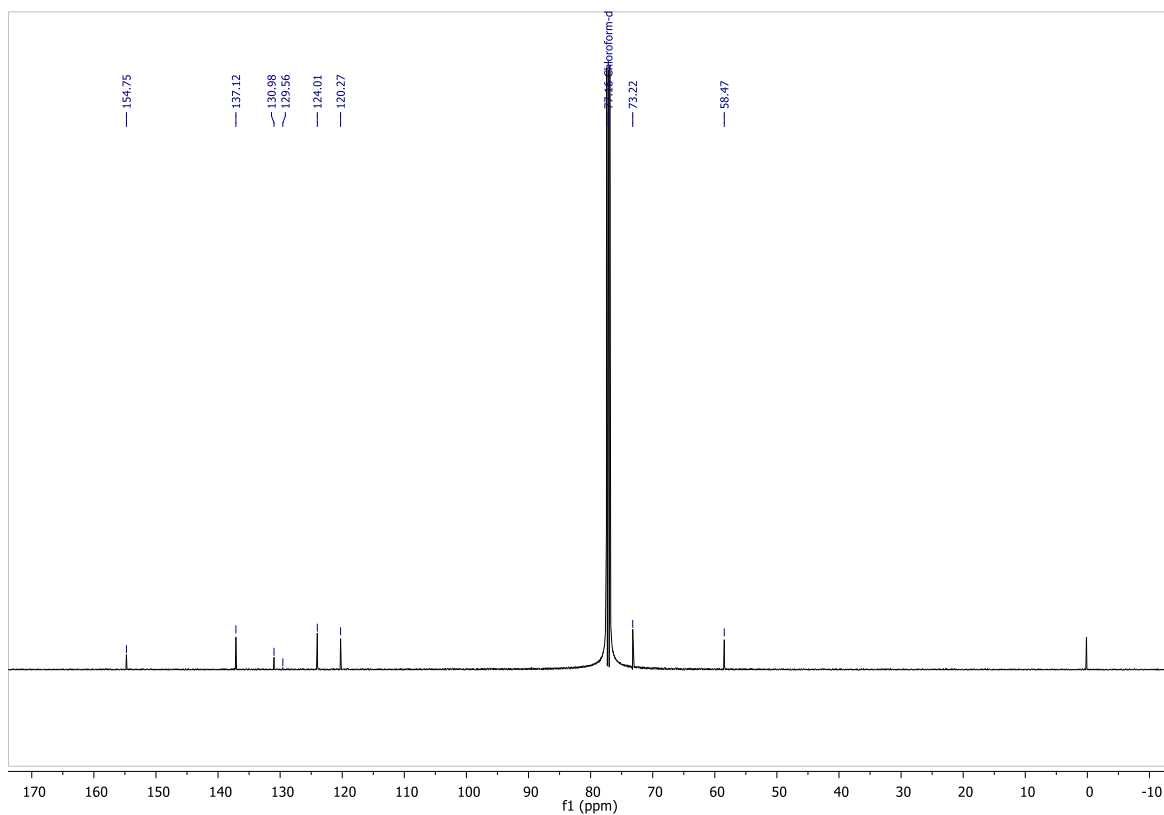
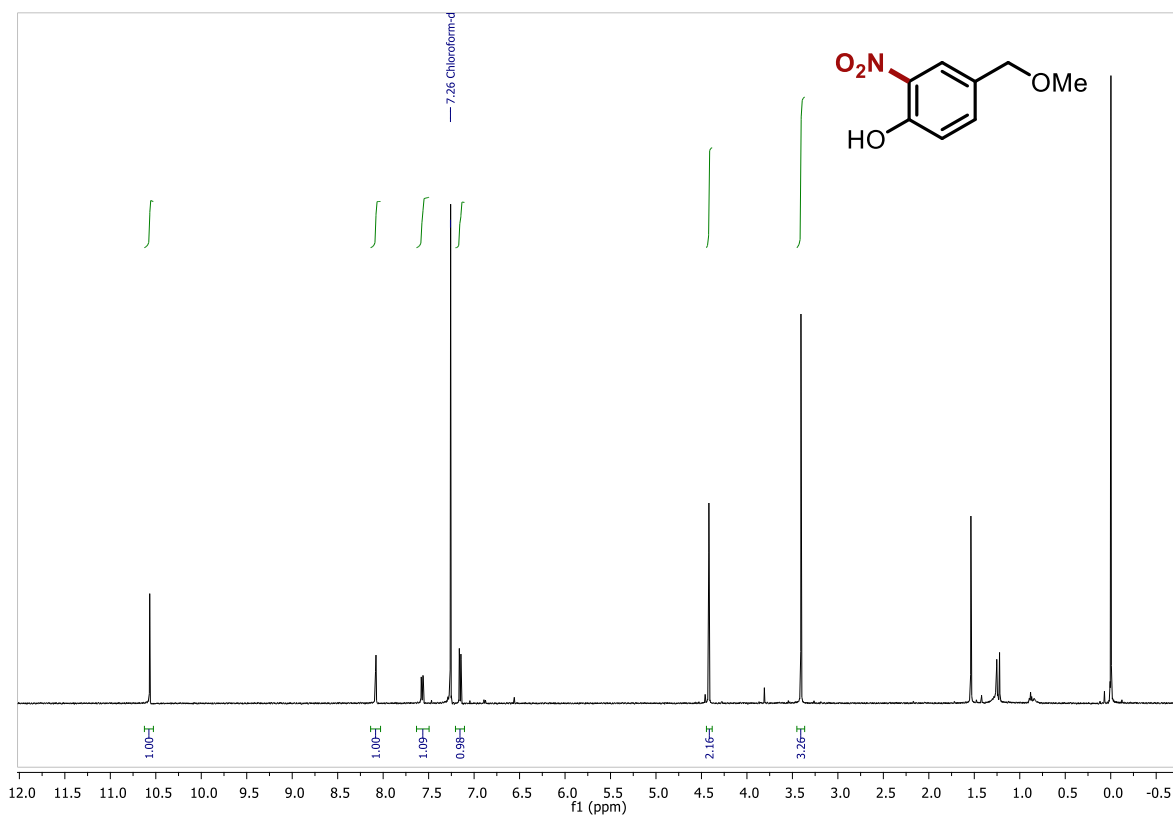
4-(2-hydroxyethyl)-2-nitrophenol (52)



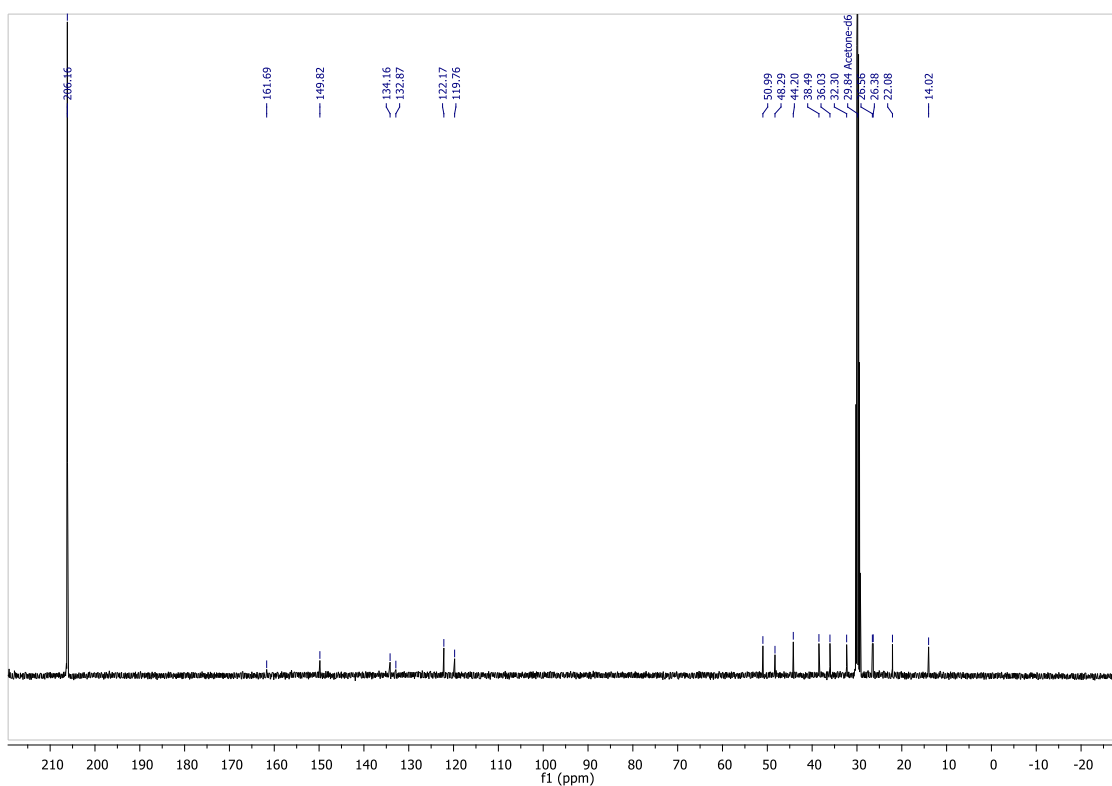
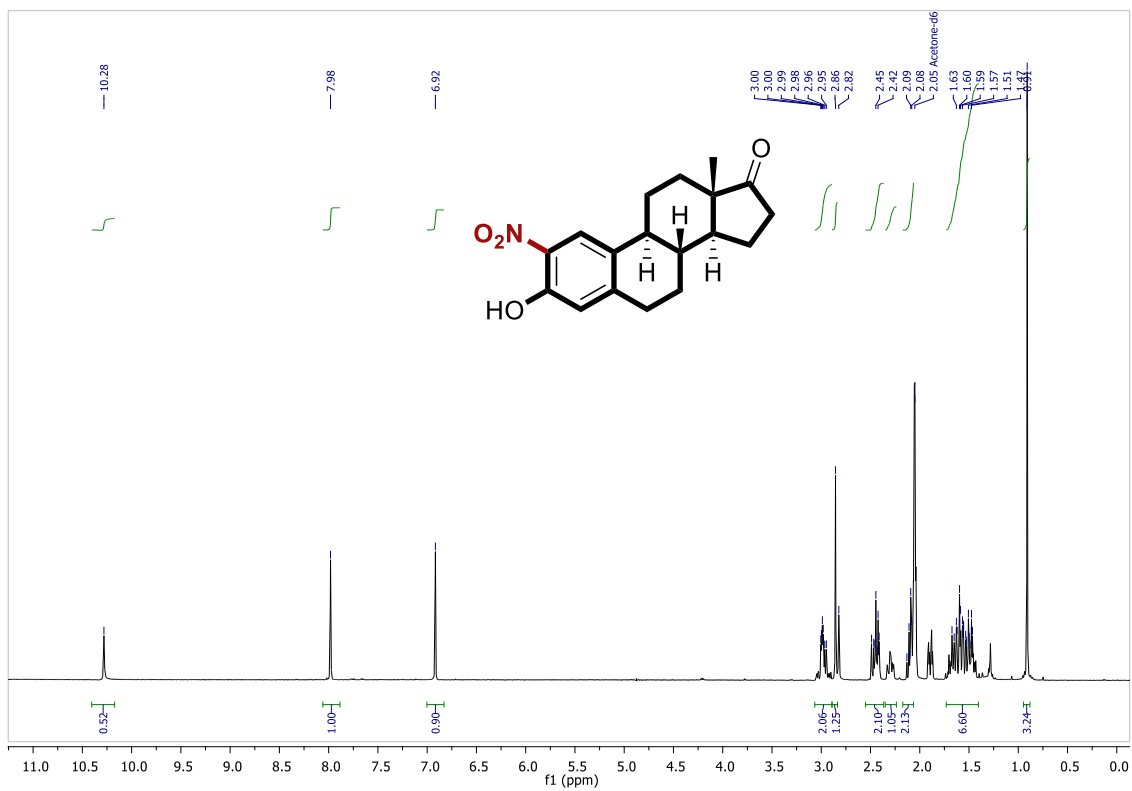
4-(hydroxymethyl)-2-nitrophenol (53)



4-(methoxymethyl)-2-nitrophenol (54)



(8*R*,9*S*,13*S*,14*S*)-3-hydroxy-13-methyl-2-nitro-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (55)



5. Computational Methodology

We have performed gas-phase geometry optimizations using the Gaussian16 rev.A.03 program.¹⁸ We used the global-hybrid, meta-GGA density-functional M08-HX developed by Zhao and Truhlar,¹⁹ in combination with the split-valence triple- ζ quality basis set with one diffuse function and one polarization function 6-311+G(d) for light elements (C, O, N, Al) but hydrogens are just described with the normal 6-311G and the LANL08+f pseudopotential for I.²⁰ Harmonic frequency calculations were also done at the same level of theory for a twofold aim: 1) To check the nature of the stationary points found (structures which are minima in energy have zero negative –imaginary– eigenvalues of the Hessian and transition states, structures which are maxima in energy, possess one and only one negative eigenvalue, which in turn, defines the reaction coordinate for each one); 2) To get the energy corrections to the electronic energy: zero-point energy, thermal and entropy corrections measured at 298.15K and 1 atm.

Finally, we have also considered solvation effects added to the electronic Hamiltonian by performing single-point calculations over the optimized geometries at the M08-HX/(LANL08+f,6-311+G*) level of theory and using the polarizable conductor-like model through the SMD variation of IEFPCM of Truhlar and workers²¹ with the dielectric standard values for acetonitrile, in concordance with our experiments. Therefore, our final reported energy values are in solvent-phase.

¹⁸ Frisch M. J.; Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Scalmani G., Barone V., Petersson G. A., Nakatsuji H., Li X., Caricato M., Marenich A. V., Bloino J., Janesko B. G., Gomperts R., Mennucci B., Hratchian H. P., Ortiz J. V., Izmaylov A. F., Sonnenberg J. L., Williams-Young D., Ding F., Lipparini F., Egidi F., Goings J., Peng B., Petrone A., Henderson T., Ranasinghe D., Zakrzewski V. G., Gao J., Rega N., Zheng G., Liang W., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Throssell K., Montgomery Jr J. A., Peralta J. E., Ogliaro F., Bearpark M. J., Heyd J. J., Brothers E. N., Kudin K. N., Staroverov V. N., Keith T. A., Kobayashi R., Normand J., Raghavachari K., Rendell A. P., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Millam J. M., Klene M., Adamo C., Cammi R., Ochterski J. W., Martin R. L., Morokuma K., Farkas O., Foresman J. B., Fox D. J., Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

¹⁹ Zhao Y., Truhlar D. G., *J. Chem. Theory Comput.* **2008**, *4*, 1849-1868.

²⁰ a) Hay P. J., Wadt W. R., *J. Chem. Phys.* **1985**, *82*, 299-310; b) Couty M., Hall M. B., *J. Comput. Chem.* **1996**, *17*, 1359-1370.

²¹ Marenich A. V., Cramer C. J., Truhlar D. G., *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

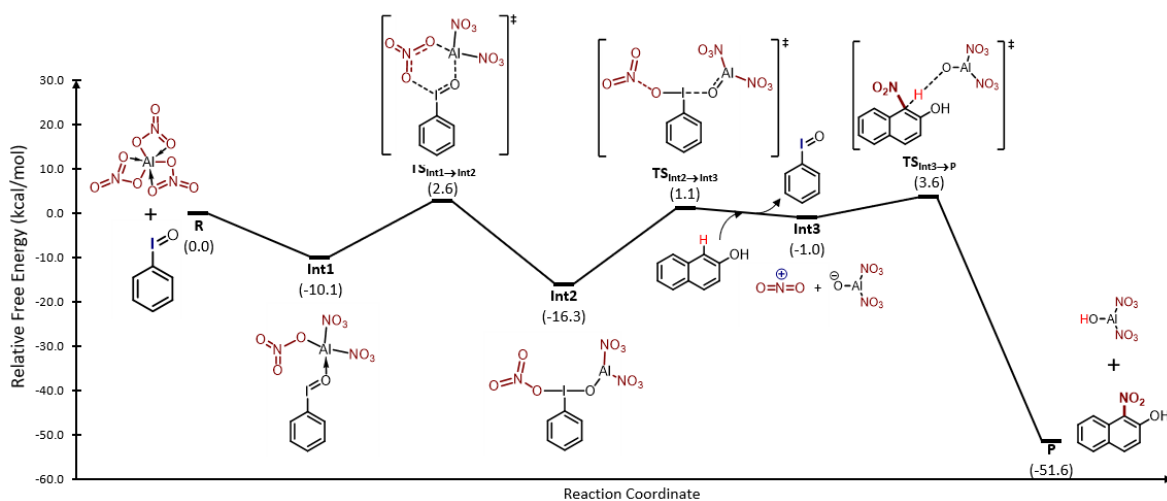


Figure S1. Gibbs free energy profile of the reaction mechanism calculated at the (SMD:MeCN)Mo8-HX/(LANLo8+f,6-311+G*) level.

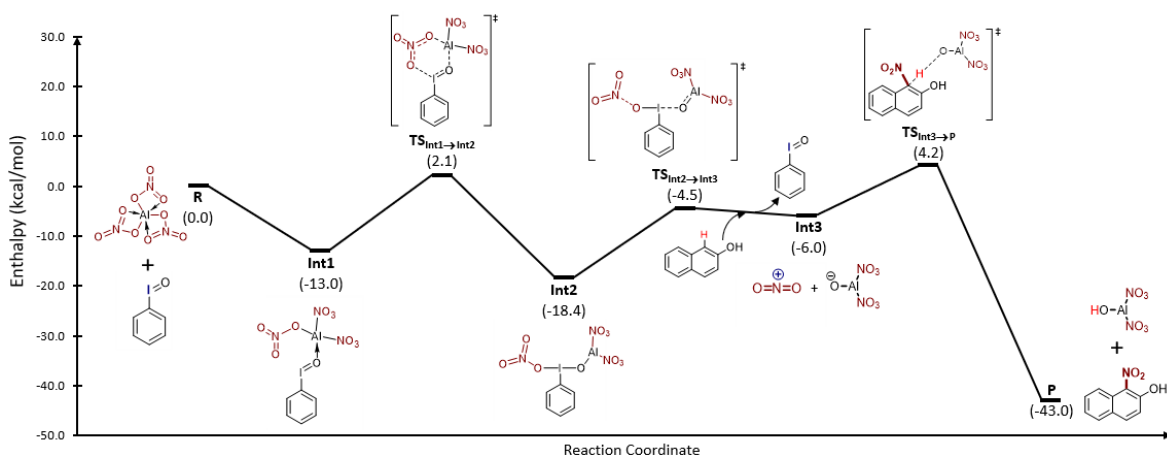


Figure S2. Enthalpy profile of the reaction mechanism calculated at the (SMD:MeCN)Mo8-HX/(LANLo8+f,6-311+G*) level.

6. Cartesian Coordinates of Optimized Structures

Table S1. Cartesian coordinates (xyz format) of all the structures involved in the proposed reaction mechanism calculated at the M08-HX/(LANL08+f,6-311+G*) level.

iodosylbenzene				Al(NO₃)₃			
E(scf) = -317.850123750 a.u.				E(scf) = -1082.80610157 a.u.			
C	0.549190	3.062856	0.000000	Al	0.000000	0.000000	0.000000
C	0.969519	1.737039	0.000000	N	0.000000	2.330846	0.000000
C	0.000000	0.745056	0.000000	N	2.018572	-1.165423	0.000000
C	-1.356357	1.017493	0.000000	N	-2.018572	-1.165423	0.000000
C	-1.755530	2.351011	0.000000	O	-3.036783	-1.753288	0.000000
C	-0.808374	3.368969	0.000000	O	1.130231	-1.235761	0.934133
H	1.288746	3.857699	0.000000	O	0.505085	1.596689	0.934133
H	2.029497	1.499485	0.000000	O	-0.505085	1.596689	-0.934133
H	-2.071032	0.197196	0.000000	O	0.000000	3.506575	0.000000
H	-2.814549	2.590166	0.000000	O	3.036783	-1.753288	0.000000
H	-1.127896	4.406291	0.000000	O	1.635316	-0.360929	-0.934133
I	0.504131	-1.314513	0.000000	O	-1.130231	-1.235761	-0.934133
O	-1.201802	-2.072022	0.000000	O	-1.635316	-0.360929	0.934133
2-naphthol				Int1			
E(scf) = -460.670118792 a.u.				E(scf) = -1400.67652677 a.u.			
C	2.685101	-0.998751	-0.000075	C	-4.739405	1.090938	1.399301
C	1.407253	-1.494483	-0.000040	C	-5.504754	1.195358	0.242077
C	0.289404	-0.622963	0.000071	C	-5.039071	0.679284	-0.961504
C	0.524089	0.783813	0.000017	C	-3.798982	0.055265	-1.018894
C	1.855398	1.263586	0.000077	C	-3.050531	-0.049696	0.149843
C	2.915259	0.394487	0.000062	C	-3.503962	0.459503	1.363726
C	-1.036307	-1.107320	0.000020	H	-5.104881	1.500307	2.335156
C	-0.591740	1.651512	0.000126	H	-6.471565	1.686735	0.278816
C	-2.096069	-0.235065	-0.000180	H	-5.635694	0.769608	-1.863089
H	-1.229412	-2.175646	0.000498	H	-3.421798	-0.331630	-1.959355
H	3.530144	-1.681014	-0.000126	H	-2.900274	0.377822	2.260787
H	1.234757	-2.567413	0.000053	I	-1.185694	-0.986571	0.076592
H	2.024531	2.337454	0.000459	Al	1.638680	0.520784	0.091581
H	3.932954	0.772608	-0.000041	O	-0.192407	0.657340	0.190395
H	-0.426175	2.725442	-0.000969	N	3.271604	0.605669	1.794479
C	-1.870507	1.159869	-0.000209	N	1.915994	2.165614	-1.569817
H	-2.718126	1.842772	0.000018	N	2.025223	-2.263049	-0.747299
O	-3.354785	-0.748098	-0.000235	O	1.381571	-1.322366	-0.015135
H	-4.001665	-0.037522	0.002768	O	3.120571	-1.991474	-1.149981
				O	1.404040	-3.282165	-0.907699
				O	1.913478	0.896157	-1.786337

O	3.549256	0.473010	0.553590
O	1.997284	0.677889	1.983321
O	4.071427	0.653438	2.662378
O	1.766028	2.429573	-0.325534
O	2.039207	2.980312	-2.416379

TS_{Int1→Int2}

E(scf) = -1400.65337765 a.u.
 $V_{\min} = -76.28 \text{ cm}^{-1}$

C	-4.739405	1.090938	1.399301
C	-5.504754	1.195358	0.242077
C	-5.039071	0.679284	-0.961504
C	-3.798982	0.055265	-1.018894
C	-3.050531	-0.049696	0.149843
C	-3.503962	0.459503	1.363726
H	-5.104881	1.500307	2.335156
H	-6.471565	1.686735	0.278816
H	-5.635694	0.769608	-1.863089
H	-3.421798	-0.331630	-1.959355
H	-2.900274	0.377822	2.260787
I	-1.185694	-0.986571	0.076592
Al	1.638680	0.520784	0.091581
O	-0.192407	0.657340	0.190395
N	3.271604	0.605669	1.794479
N	1.915994	2.165614	-1.569817
N	1.743408	-2.801795	-0.785675
O	1.283149	-1.761742	-0.049681
O	2.863082	-2.725035	-1.205355
O	0.953006	-3.698549	-0.931594
O	1.913478	0.896157	-1.786337
O	3.549256	0.473010	0.553590
O	1.997284	0.677889	1.983321
O	4.071427	0.653438	2.662378
O	1.766028	2.429573	-0.325534
O	2.039207	2.980312	-2.416379

Int2

E(scf) = -1400.68451277 a.u.

C	1.488467	2.671061	-2.026359
C	1.569491	3.510639	-0.920617
C	1.527042	2.985800	0.366184
C	1.398339	1.614546	0.563131
C	1.311751	0.799225	-0.558594
C	1.357577	1.297930	-1.854534
H	1.528444	3.081084	-3.030331
H	1.670583	4.581819	-1.062857
H	1.597745	3.641004	1.228280
H	1.388655	1.195910	1.561766
H	1.296394	0.637075	-2.711767
I	1.047766	-1.263680	-0.296276
Al	-2.288581	-0.218386	0.043996
O	-0.944088	-1.064489	-0.542366
N	-2.040569	1.901055	1.026865
N	-4.397582	-1.210586	-0.158303
N	3.908014	-1.031512	0.823241
O	3.244707	-1.397654	-0.279912
O	5.099723	-1.177222	0.784309
O	3.262696	-0.583604	1.754098
O	-3.749769	-0.727152	-1.149878
O	-2.561294	1.653031	-0.137540
O	-1.680437	0.819374	1.606089
O	-1.920257	2.983813	1.473394
O	-3.731895	-1.055201	0.948877
O	-5.452752	-1.727239	-0.221112

TS_{Int2→Int3}

E(scf) = -1400.65362130 a.u.
 $V_{\min} = -613.25 \text{ cm}^{-1}$

C	1.488467	2.671061	-2.026359
C	1.569491	3.510639	-0.920617
C	1.527042	2.985800	0.366184

NO₂⁺

E(scf) = -204.567238255 a.u.

N	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.111185
O	0.000000	0.000000	-1.111185

Int3

C	1.398339	1.614546	0.563131	E(scf) = -877.896092292 a.u.			
C	1.311751	0.799225	-0.558594	Al	-0.000059	0.936691	-0.000090
C	1.357577	1.297930	-1.854534	O	-0.000408	2.568069	-0.000054
H	1.528444	3.081084	-3.030331	N	1.932315	-0.558110	0.045343
H	1.670583	4.581819	-1.062857	N	-1.932195	-0.558329	-0.045272
H	1.597745	3.641004	1.228280	O	-1.666974	0.085589	0.999808
H	1.388655	1.195910	1.561766	O	1.080120	-0.354808	0.992360
H	1.296394	0.637075	-2.711767	O	1.666971	0.085598	-0.999853
I	1.047766	-1.263680	-0.296276	O	2.873916	-1.287126	0.180422
Al	-2.521715	-0.195072	0.015193	O	-1.079853	-0.355208	-0.992238
O	-1.177222	-1.041175	-0.571169	O	-2.873781	-1.287353	-0.180361
N	-2.273703	1.924369	0.998062				
N	-4.630716	-1.187272	-0.187106				
N	4.148879	-0.898556	1.223826				
O	3.244707	-1.397654	-0.279912				
O	5.306789	-1.118757	0.992152				
O	3.335251	-0.483110	2.029410				
O	-3.982903	-0.703838	-1.178681				
O	-2.794428	1.676345	-0.166343				
O	-1.913571	0.842688	1.577286				
O	-2.153391	3.007127	1.444591				
O	-3.965029	-1.031887	0.920074				
O	-5.685886	-1.703925	-0.249915				

TS_{Int3→Prod}				Prod			
E(scf) = -1543.37922264 a.u.				E(scf) = -665.033235030 a.u.			
V _{min} = -1052.42 cm ⁻¹							
C	-3.426656	-0.296714	0.038537	C	-3.426656	-0.296714	0.038537
C	-2.756105	0.898416	-0.025380	C	-2.756105	0.898416	-0.025380
C	-1.347148	0.942454	-0.034249	C	-1.347148	0.942454	-0.034249
C	-0.583917	-0.262126	0.006015	C	-0.583917	-0.262126	0.006015
C	-1.307124	-1.475797	0.082828	C	-1.307124	-1.475797	0.082828
C	-2.685024	-1.483459	0.100935	C	-2.685024	-1.483459	0.100935
H	-1.292970	3.099401	-0.118125	H	-1.292970	3.099401	-0.118125
H	-4.511426	-0.323714	0.046519	H	-4.511426	-0.323714	0.046519
H	-3.301566	1.837359	-0.063395	H	-3.301566	1.837359	-0.063395
C	-0.687754	2.198143	-0.074200	C	-0.687754	2.198143	-0.074200
C	0.855140	-0.135266	0.007974	C	0.855140	-0.135266	0.007974
H	-0.781851	-2.415875	0.122513	H	-0.781851	-2.415875	0.122513
H	-3.199914	-2.437372	0.164074	H	-3.199914	-2.437372	0.164074
C	1.467760	1.130923	0.014844	C	1.467760	1.130923	0.014844
C	0.665658	2.294656	-0.043251	C	0.665658	2.294656	-0.043251
H	1.181241	3.248071	-0.058785	H	1.181241	3.248071	-0.058785
				O	2.770882	1.353184	0.055382

